THERMAL INSULATION OF POLYMERIC COMPOSITES USING SURFACE TREATMENTS

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DECLARATION OF AUTHORSHIP

I declare that the work described in this PhD thesis has not previously been presented in any form to the University or to any other institutional body, whether for assessment or for other purposes. I confirm that the intellectual content of the work is the result of my own effort and of no other person.

Signed ………………………………..

Date ………………………………..
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Fibre-reinforced polymeric composites for structural applications are required to conform to specific fire performance requirements and to retain their mechanical integrity after exposure to heat/fire. Many polymeric composites will lose their structural integrity when exposed to temperatures close to the glass transition temperature of the resin matrix. The most effective technique of protecting these materials against heat and fire is the use of surface coatings, which can inhibit or reduce the heat transfer from the fire/heat source to the underlying structure. In this PhD, novel thermal barrier coatings and techniques of their application on the surface of glass fibre-reinforced epoxy (GRE) composites were developed. These include: (1) commercially available intumescent coatings applied by paint brush and roller (2) nanoclays, dispersed in a solvent and sprayed on plasma activated GRE laminate surfaces (3) ceramic nano/microparticles dispersed in a flame retardant resin, applied by painting or K-bar application and (4) chemical coating obtained by applying phosphorus containing monomers (vinyl phosphonic acid) on a GRE surface by paint brush and polymerisation using UV radiation.

Surface characterisation was carried out on each coating by scanning electron microscopy (SEM) and a water drop test. These results showed that the application method used plays an important role in determining the uniformity of the coating. Plasma treatment increased the hydrophilicity of the GRE composite surface, while in the presence of a resin binder, the coating established a hydrophobic surface. The effect of these coatings on the flammability of the composites was studied by a cone calorimeter at different heat fluxes, and the thermal barrier effect of the coatings was measured by insertion of thermocouples into the laminate during the cone experiments and measuring the time for the back surface temperature to reach the glass transition temperature of the resin. Intumescent coatings, as expected, showed the best performance and were used to set a benchmark for the performance of the other coatings. The nanoparticle and micro-ceramic particle coatings can act as thermal barriers. However, their concentration on the
surface of laminates was not high enough to provide effective thermal protection for an extended period of time. The chemical (poly (vinyl phosphonic acid)) coating provided the best thermal barrier of the coatings due to its ability to form an intumescent char.

Three point blending flexural and impact tests were used to study the effect of the coatings on the mechanical properties of the laminates. The contribution of the coating to the impact and flexural modulus of the laminates is related to the thickness of the coating and its mechanical properties. Thus, thin coatings showed better results than thick coatings. Each coating had a minimal effect on the mechanical properties of the GRE composite, while they improve the retention of mechanical property after exposure to heat, with the chemically coated samples performing the best, due to the formation of a thick intumescent char.

A tape pull was performed to study the adhesion of the coatings on the GRE surfaces. All coatings containing resin binder or polymerized on the GRE surfaces were durable and did not peel off. The durability to water was tested by a water soak test. The nano/micro particulate ceramic coatings showed the best performance, whereas the chemical coatings showed the worst behaviour due to the highly hydrophilic nature of the poly (vinyl phosphonic acid).
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Chapter 1

INTRODUCTION

Fibre-reinforced polymer (FRP) composites, made by embedding structural fibres (of high strength and stiffness) in thermoset polymers (resins), are becoming popular alternatives to metals due to their low cost, lightweight, resistance to environmental variants and excellent mechanical properties. Unfortunately, composites of this type have relatively poor heat and fire resistance because of the organic nature of the matrix [1]. Their response to heat depends upon the type and intensity of the heat source. At temperatures below the glass transition temperature of the resin, the resin is unaffected by heat and there is little effect on mechanical properties. On reaching the glass transition temperature, the matrix softens and the composite laminate starts losing its mechanical properties. This concern has led to efforts for finding ways to reduce heat transfer through the thickness of the laminate on exposure to heat and fire. This is the focus of this work.

In this chapter, the constituents of a fibre-reinforced polymer (FRP) composite and their effect on the flammability, mechanical properties and structural integrity during exposure to heat/fire are reviewed. Different approaches to reduce the flammability of polymeric composites and their shortcomings are also summarised leading to the aim and objectives of this PhD project. The scope and structure of the thesis has also been discussed.

1.1 Fibre reinforced polymeric composites

Although the concept of composite materials has always existed in nature and has been used by humans since prehistoric times when straw or animal hair were used to reinforce mud houses. The term “fibre-reinforced polymer (FRP) composite material” was introduced during World War II. The earliest FRP materials used glass fibres embedded in polymeric
resins that were made available by the burgeoning petrochemical industry for construction applications [2]. In the 1960s, FRP materials were first commercialised to meet the higher performance challenges of the defence and aerospace industries. With newer manufacturing processes and decrease in cost, the use of FRP composite materials became more extensive from 1970s onwards, due to their good mechanical properties, light weight, easy processability, resistance to environmental changes and low cost. As substitute materials for metals, the FRP materials are widely used in aerospace (e.g. space shuttle and satellite systems), automotive (e.g. body panels, leaf springs, drive shafts, bumpers, doors and racing car bodies) and marine industries (e.g. boat bodies, canoes and kayaks). These industries have recognised that FRP materials display high strength-to-weight ratios in comparison with most metals and alloys, meaning that FRP composite structures offer the potential to be significantly lighter than structures made from conventional materials [3,4].

Generally, a fibre-reinforced polymer is a composite material consisting of a polymer matrix and fibre-reinforcing matrix. The main purpose of the fibre-reinforcement is to improve the mechanical properties of the polymer matrix system. For structural composites usually glass, carbon or aramid fibres are used in particular reinforcement forms such as filaments, chopped strands, woven fibre rovings or mats [5]. These fibres have very high strengths and modulii, which are much higher than traditional polymer materials. Table 1.1 gives a comparison of the mechanical properties of some the important commercial reinforcing fibres.

**Table 1.1: Properties of composite reinforcing fibres [6]**

<table>
<thead>
<tr>
<th>Fibre</th>
<th>E (GPa)</th>
<th>σ_b (GPa)</th>
<th>ρ (kg/m³)</th>
<th>E/ρ (MJ/kg)</th>
<th>σ_b/ρ (MJ/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>E-glass</td>
<td>72</td>
<td>2.4</td>
<td>2,540</td>
<td>28</td>
<td>0.95</td>
</tr>
<tr>
<td>Aramid</td>
<td>124</td>
<td>3.6</td>
<td>1,440</td>
<td>86</td>
<td>2.50</td>
</tr>
<tr>
<td>HS graphite</td>
<td>253</td>
<td>4.5</td>
<td>1,800</td>
<td>140</td>
<td>2.50</td>
</tr>
<tr>
<td>HM graphite</td>
<td>520</td>
<td>2.4</td>
<td>1,850</td>
<td>281</td>
<td>1.30</td>
</tr>
</tbody>
</table>

Note: E is the modulus of elasticity, σ_b is the tensile strength, and ρ is the density

In particular applications, such as marine and automotive composite structures, E-glass fibre-reinforcements are primarily used. By comparison, the aerospace industry relies more on carbon and aramid fibres. However, these fibres and other specialty reinforcements are also employed in the marine and automotive fields where structures are highly engineered for optimum efficiency. Typically these fibre-reinforcements are impregnated by a polymer
matrix to create structural laminates. The polymer matrix transfers loads to the fibre-reinforcements and holds them in place to form the desired shape. The combination of these matrices offers high strength-to-weight or modulus-to-weight ratios to the finished composite materials. The polymer matrix can be either thermoplastic or thermosetting, both of which differ in physical and chemical terms. A thermosetting resin is crosslinked during curing, whereas thermoplastics (polypropylene, nylon etc.) contain no crosslinking bonds and hence, move freely when the polymer reaches its melting point. The different classes of thermoset resins find applications in different industries. The marine industry has generally based its structures on unsaturated polyester resin. For automotive and transportation applications, the trend is vinyl ester and bi-functional epoxy resins, while, tri- or tetra-functional epoxy and phenolic resins are mainly used in aerospace applications. The fabrication and shaping of composites into finished products often combines the formation of the material itself during the fabrication process [7]. The important processing methods for thermosetting polymer composites are hand lay-up, bag moulding process, filament winding, pultrusion, bulk moulding, sheet moulding and resin transfer moulding.

1.2 Flammability and structural integrity of polymeric composites on exposure to fire

As mention above, a reinforced polymer composite structure comprises fibre and resin. Both of these components have different thermal stabilities and responses to fire. For marine, automotive and aerospace applications, most composite structures are made from less-combustible fibre (e.g. glass, carbon or aramid fibres) and conventional polyester or epoxy resins [8,9].

Table 1.2: Thermal stabilities of some thermosetting matrix polymers

<table>
<thead>
<tr>
<th>Type of thermosetting polymer</th>
<th>Glass transition temperature, $T_g$ (°C)</th>
<th>Maximum processing temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyester</td>
<td>80-100</td>
<td>50</td>
</tr>
<tr>
<td>Epoxy</td>
<td>120-180</td>
<td>150</td>
</tr>
<tr>
<td>Phenolic</td>
<td>130-180</td>
<td>200</td>
</tr>
<tr>
<td>Bismaleimide</td>
<td>180-200</td>
<td>220</td>
</tr>
<tr>
<td>Polyimide</td>
<td>300-330</td>
<td>280</td>
</tr>
</tbody>
</table>
Therefore, the burning behaviour of a polymeric composite laminate in such applications depends upon the thermal stabilities and responses to fire of the organic polymer resin matrix [10]. Polymers like epoxy resin are degraded by exposure to temperatures above about 120°C, as illustrated by the data in Table 1.2 [11].

Generally, all polymer materials burn by exothermic reactions. The actual process of combustion is very complex, but broadly follows four main stages [12].

1. **Heating of the polymer**: The ignition source heats the bulk polymer to create a rise in temperature. The heated polymer starts to be softer and then possibly distort above its glass transition temperature ($T_g$). They will start to degrade generally through the formation of free radicals, under the influence of the heat source and any oxidant present.

2. **Polymer Decomposition**: The polymer starts to degrade rapidly into a range of lower molecular weight decomposition products. Typical products at this stage are combustible gases and liquids, charred solids and possibly smoke.

3. **Ignition**: The combustible gases, in the presence of sufficient oxygen and the ignition source, ignite to start combustion. It is the combustible gases and liquids that burn and not the bulk material.

4. **Combustion**: The burning gases produce a combustion layer at or near the surface of the bulk polymer and the process can become self-sustaining if it produces sufficient energy to maintain polymer decomposition and fuel production. Depending on the type of polymer, the combustion stage produces flames (which can propagate), charred surface layers and can be accompanied by the emission of smoke and toxic gases.

The reinforcement cannot retard or stop the chemical degradation of the polymer composite upon exposure to heat or fire, but the degradation of the polymer is associated with a fall in strength and an increase in time-dependent deformation of the composite. When dealing with the behaviour of fibre-reinforced polymer composites in fire, combustion is usually accompanied by delamination, where the resin part of the composite decomposes and the fibres are torn apart from the matrix, resulting in significant loss of mechanical properties of the laminate [13,14,15]. This leads to concerns about their structural integrity and mechanical properties during and after exposure to fire. Several investigators have attempted to study the behaviour of polymer composites subjected to thermal exposure. For instance,
Gardiner et al. [16,17] have reported that on exposing a glass reinforced polyester (GRP) composite to a kerosene fuel tray fire of approximately 30 kW/m² radiative intensity for 10 min, ignition occurred after 30 s. The main types of fire damage to the composite plates following ignition were charring of the polyester matrix, cracking and delamination. This resulted in 50 % reduction in flexural strength, 60 % in rigidity and 70 % in compressive strength. Moreover, the stiffness and failure load of the composites decreased rapidly with increasing heat flux, or exposure time, mainly due to rapid thermal degradation of the resin matrix. Sorathia et al. [18], measured the flexural strength of several types of composites after exposure to a heat flux of 25 kW/m² for 20 min. The results showed a reduction of more than 75% in flexural strength compared to the original strength of unburnt samples. Similar experiments were also conducted by Mouritz and Mathys [19,20,21] for glass reinforced polyester, vinyl ester and phenolic laminates exposed to heat fluxes between 25 and 100 kW/m² for exposure times up to 30 min. At 50 kW/m² heat flux, the post-fire tensile, compressive and flexural properties dropped rapidly (≥ 50 % reduction) after heat exposure times between 750 to 1000 s. After 1800 s the stiffness and failure load decreased by 80 to 90% of their original values. The thickness of the char layer decreased and delamination increased, with increasing exposure time and heat flux. It is clear that it is very desirable to improve the resistance to burning of these materials in order to preserve their structure and mechanical properties during and after exposure to fire.

1.3 Different approaches to reduce flammability of polymer composites

To overcome the poor fire and heat resistance of FRP composites, the science and technology of flame retardant polymer composites has extensively grown since the late 1990s. Several methods have been established to improve the poor heat resistance of the resin matrix in the polymer composites. These are summarised below.

1.3.1 Incorporation of flame retardant chemicals

Flame retardant chemicals may either be reacted with the resin in such a way that they are incorporated into the backbone of resin (built chemically into the polymer molecule) or can be physically added as additives (not chemically reacted with the polymer) [22,23]. Generally, flame retardants act by one of the following three different approaches: (1)
modifying the decomposition pathway of the polymer and causing “char” formation in the pyrolysis zone; (2) decomposing to produce nonflammable gases such as water vapour, carbon dioxide, ammonia etc. to cool the pyrolysis zone; and (3) prohibiting the combustion process in the vapour phase by quenching free radicals [24]. During fibre-reinforced polymer composite fabrication, flame retardant additives, such as tris-(tribromophenyl) phosphate, polyphosphate, melamine phosphate, ammonium phosphate can be dispersed into the resin matrix prior to laminate lay-up [25]. However, the introduction of flame retardant additives in a polymer composite is required in very high concentrations (>20%) in order to be fully effective, leading to undesirable changes in physical and mechanical properties of the composites [26]. On the other hand, phosphorus-containing monomers, such as diethyl-acryloxyloxy ethyl phosphorus, DOPO (dihydro oxa phosphaphenanthrene oxide) and phosphorus amidate, can be added as monomers during the polymerisation process and hence, become an integral part of the polymer.

1.3.2 Nanocomposites

Nanocomposites, which inherently increase thermal stability and reduce flammability by physical means, have received much attention in the last few years as potential alternatives to conventional flame retardants. Nanocomposites also give additional properties, such as improved mechanical properties (modulus/strength) [27]. A variety of nanoparticles can be used to fire retard polymer composites. Examples include SiO₂, Al₂O₃, TiO₂, layered nanosilicates (clays), graphite, multi-walled carbon nanotubes, single-walled carbon nanotubes and carbon nanofibres. The nanocomposites can be obtained by dispersing nanoparticles into the polymer matrix. The most researched nanoparticles in this field are layered silicate nanocomposites. The flame retardant effect of these layered silicate nanocomposites is believed to be due to formation of a thermally insulative silicate layer on the surface of the burning polymer, which slows down the burning process. Moreover, the char formation from these layered silicates is obtained by low loadings (≤ 5 wt%), due to their platelet geometry, high aspect ratio and very high specific surface area [28,29,30]. These are environmentally friendly and highly efficient when compared to conventional flame retardants.
1.3.3 Use of high performance fibres

The use of high performance fibres, which are inherently heat and fire resistant, renders the composite less flammable compared to the neat resin [31]. Glass, carbon, ceramic and aramid fibres are mostly used for structural composites. Although, these fibres are non-flammable, they do not provide fire retardancy to the whole composite structure. Some fibres such as ceramic fibres, due to their high densities do increase the composite weight.

1.3.4 Surface coatings

Another efficient way to protect the composites against fire/heat without significantly affecting their physical and mechanical properties is the use of surface coatings. Different types of coating can be used as described in following discussions.

1.3.4.1 Flame retardant coatings

Traditional flame retardant coatings typically utilize compounds that contain flame retardant additives or fillers, such as halogen-containing flame retardants (i.e. chlorine or bromine), phosphorus-containing flame retardants and inorganic compounds (i.e. aluminium hydroxide (ATH) and zinc borates). In most of cases, these flame retardant coatings usually help inhibit the flame spread or preferably work in the gas-phase by acting as free radical scavengers [32,33].

1.3.4.2 Intumescent coatings

Intumescent coatings are the most common coatings used for composites, and are applied by painting or spraying of chemicals onto the surface of the composite. Intumesence is defined as the swelling of certain substances, when they are heated. Intumescent material on exposure to heat/fire is designed to expand to form an insulating and fire resistant char cover between the fire and the underlying laminate. This charred layer acts as a thermal insulator/barrier for the underlying laminate by physically stopping the heat and oxygen penetrating to the materials, thereby maintaining the structural integrity of the laminate. The basic components of these intumescents are a carbon source, a blowing agent and an acid source [34]. The formulation of the coating has to be optimised in terms of physical and chemical properties in order to form an effective protective char. The performance of an
intumescent coating depends upon the thickness of the coating and the expanded char [35,36]. A thick expanded char is more effective in prevention of the penetration of heat compared to a thin expanded char layer. Apart from intumescent coatings, flame retardant chemicals can also be used in gel coats [37] and along with ceramic coatings as hybrid systems [38].

1.3.4.3 Thermal insulative mat/sheet

The term thermal insulation materials refer to the ability of a material either to reduce or block the heat transmission through its layers. By protecting the surface from heat transmission, they also preserve the original mechanical properties of composites [39]. Thermal insulative materials include intumescent mats, ceramic mats and insulative fabrics. These can be used as the top layer of composite laminates by impregnating with resin during lay-up or bonded to the surface of the already prepared composite laminate using a small amount of resin as a bonding material [40]. The only drawback is that they add extra weight.

1.4 Research aims and objectives

Although all the modification of the resin matrix methods reported in the literature (see Sections 1.3.1 to 1.3.3) have been used to improve composite fire resistance, they only change the burning behaviour of the composite, but do not affect the softening of a typical structural composite matrix. The softening of the composite structure plays a very important role in the reduction of the mechanical properties of composites, when the resin softens near its glass transition temperature, the mechanical properties of the composite laminate decrease significantly. Consequently, there is a continual search for flame retardant systems that protect the composite materials against fire/heat without modifying their intrinsic properties and can also stop the softening of the composite resin matrix. The use of surface coatings (see Section 1.3.4) can improve the thermal stability and flammability properties of the composite without the disadvantages mentioned above. However, they have certain disadvantages for instance, the intumescent coating requires a thick coating layer (> 1mm coating thickness), which may not be applicable in some applications. Thermal insulative mat/sheets, such as intumescent mats, may add to weight to the composite and may absorb fuel in case of an accident.
The main aim of this work is to develop novel surface coatings to improve the thermal stability and flammability properties of glass fibre-reinforced epoxy (GRE) composites with thermal barrier effects that do not suffer from these disadvantages. The following objectives are identified to achieve the aim of this work.

1) To identify chemicals and materials that can be used as a thermal surface insulation barrier for polymer composites and select/develop those coating systems, which would enable a given composite structure to survive a defined thermal threat for a specified heating time.

2) To explore and develop various methods of surface treatments that can be used for polymer composites.

3) To fabricate a series of polymer composite laminates and apply surface coatings following the outcome of (2).

4) To study the physical, thermal insulative and mechanical properties of these coatings.

5) To study the flammability and mechanical performance of these produced composite laminates.

The surface coatings developed during this study are divided into four main types.

- Intumescent coatings
- Nanoparticle depositions
- Ceramic micro-particle coatings
- Chemical surface coating by polymerising vinyl phosphonic acid (VPA) monomer on the laminate surface

The methods of application include normal painting and spraying onto the composite laminate surfaces using either an atmospheric plasma technique or a flame retardant binder, so that the coatings are physically and/or chemically bound to the organic resin of the laminate surface.
1.5 Thesis layout

**Chapter 1:** The introductory chapter.

**Chapter 2:** This chapter presents a comprehensive literature review of surface coatings in general, and also, in particular, the most commonly used for thermal barrier and fire resistance applications for various substrates. Techniques used for applying surface coatings on polymeric substrates are also reviewed.

**Chapter 3:** In this chapter, experimental details of composite preparation, application of different coatings on their surfaces and characterisation methods used for their physical, mechanical and thermal barrier properties are presented.

**Chapter 4:** This chapter focuses on the outcome of intumescent coatings on GRE composites. Three commercial coatings of different thicknesses have been applied to the composite surfaces. The flammability of the composites and thermal barrier efficiency of those coatings are determined by a cone calorimeter in order to understand the burning behaviour of GRE composite structures and the thermal barrier efficiency of these three intumescent coatings. These fire resistance and thermal barrier properties are required as a benchmark to indicate the minimum required performance of other coatings being developed during this work.

**Chapter 5:** The deposition of an organically modified nanoclay on the GRE composite laminates as a ceramic coating to improve flammability of the composites is presented. Two different approaches for deposition of the nanoclay on composite surface are described: 1) the use of the atmospheric argon plasma and 2) the use of a resin binder. The effects of plasma treatment on GRE composite surface are investigated by IR-ATR and a water drop test. The surface morphology of each coated surface is studied by SEM. The adhesion between the coating and the GRE substrate has been studied by the tape pull method and the durability to water by the water-soak test. The flammability and thermal barrier properties of these coated composites are also investigated. Conclusions drawn from all the results are given at the end of this chapter.
Chapter 6: In this chapter, the deposition of ceramic micro/nano particles on GRE composite surfaces as thermal barrier coatings are reported. The effects of these ceramic coatings on the physical, thermal barrier properties and flammability of composite laminates have been studied by similar techniques as mention in Chapter 5. The effect of heat on mechanical property retention after exposure to radiative heat (cone calorimeter) has also been studied by the three point bending test.

Chapter 7: Synthesis and characterization of the novel coating for polymerisation of phosphorus containing monomers, such as vinyl phosphonic acid (VPA), on GRE composite surfaces are discussed. A major part of this section focuses on the VPA monomer tailoring of the composite surface by UV polymerisation. The effects of this VPA polymerisation coating on thermal stability, physical and mechanical properties of the GRE composite laminates were also studied and discussed in a similar way to the previous chapter.

Chapter 8: This chapter summarises the results obtained from three types of coatings developed in this research and compares different coatings in terms of their thermal barrier effectiveness, durability and mechanical properties. The recommendations for further work are also included.

1.6 References


Chapter 2

LITERATURE REVIEW

The aim of this chapter is to provide the basic background associated with surface coatings, their thermal barrier and fire resistance properties and the general application methods that are employed. A general introduction to the typical techniques used for surface coating deposition on polymeric substrates is also provided.

2.1 General aspects of surface coatings

A surface coating is the general description of any material applied as a thick or thin continuous layer (e.g. paint, lacquer, enamel, varnish, etc.) onto a surface of an object, normally called a substrate, and appears as either a continuous or discontinuous film after drying [1]. In general, surface coatings have been used throughout history for decorative and/or protective purposes on a wide variety of substrates: organic substrates (e.g. plastics, resins, rubbers and woods), non-metallic inorganic substrates (e.g. glass and ceramics) and metallic substrates (e.g. steel, aluminium, nickel and copper). Over the years, the function of the surface coatings has becomes more complex. Several materials have evolved to meet higher challenges as functional coatings, which possess an additional functionality apart from the aforementioned properties of a coating [2]. For example, coatings that are applied to improve the surface properties of the substrate (e.g. specific wettability, scratch or abrasion resistance, transparency, defined permeability) or to protect the bulk properties of the substrate (e.g. chemical resistance, anti-microbial, barrier, thermal resistance and fire resistance) or to provide special functions (e.g. reflecting, diffractive, sensor, self-cleaning, self-healing, luminescence, acoustic and wave absorbing) [3,4]. These functional coatings are extensively used on high performance materials used in wide variety of industrial sectors such as textiles, automotive, aerospace, transportation equipment and machinery.
2.1.1 Types of surface coatings

A coating's effectiveness depends on the appropriate choice of coating materials. For instance, inorganic compounds generally have excellent abrasion resistance, thermal resistance and high density, but are brittle and require high processing temperatures; organic compounds are mechanically flexible and tough, but have poor abrasion and thermal resistance [5]. In general, the coating materials can be classified by using several criteria based on their field of application, on the nature of their bonding or on their chemical composition. Here different types of coatings based on their chemical composition are discussed.

2.1.1.1 Metal coatings

Metal coatings can be defined as thin films of metallic material bonded to a substrate. They are usually applied as a protective layer over metallic substrates (e.g. steel, magnesium alloys, aluminium, etc.). However, sometimes non-metallic substrates such as plastics are coated to give a metallic appearance. The application of metal coatings for the protection of metallic substrates may be required for one or more of reasons, such as (1) to prevent or reduce corrosion, (2) to modify the physical or mechanical properties and (3) to achieve and maintain some desired decorative effect of the metallic substrates. In all cases of a metal coating/metal substrate system, the metal coatings are typically used in the main to provide long term corrosion resistance in a severe environment [6].

2.1.1.2 Ceramic coatings

Ceramics, such as pure oxides of alumina (Al$_2$O$_3$), zirconia (ZrO$_2$) and magnesia (MgO), are widely used for ceramic coatings because of their excellent wear resistance, lightweight and low conductivity [7]. Thin ceramic coatings are extensively used on metal substrates, in particular metallic engine parts, to improve heat insulation, corrosion and oxidation resistance in those engine parts, and also prevent coated materials from decomposing under high temperatures [8,9]. The ceramic coating and its applications are described in more detail in Section 2.2.
2.1.1.3 Polymer coatings

Conventional polymer coating formulations, such as paints, varnishes and inks consist of a binder, a filler (or particle), a solvent/carrier, pigments, and additives [10,11]. In this formulation, the polymer functions as the binder material providing a matrix in which all other constituents are solubilised or dispersed [12]. The binder is generally based on organic polymers and inorganic polymers, which can be either thermoplastic or thermosetting. However, most binders are thermoset type polymers because of their viscosity and reactive structure [13]. The choice of resin depends upon the application, e.g. phenol-formaldehyde resins, polyesters resins, epoxy resins and acrylic resins are mostly used for decorative and functional applications, while silicone based resins are mainly applied for protective purposes [14]. In general, polymer coatings involve the application of a thin polymer film onto a substrate material. Depending on their composition, polymer coatings can be divided into three groups [15].

1) Solvent-borne coatings consisting of a binder, additives and pigments that are dissolved or dispersed in organic solvents.
2) Water-borne coatings, which contain the ingredients similar to those used for solvent-borne paints, but dispersed in water.
3) Solvent-free (100% solid) coatings, which do not contain any solvent or water and the ingredients are dispersed directly into the binder.

Recently, organic-inorganic hybrid polymer coatings, such as epoxy modified polysiloxane and polysiloxane polyurethane compositions, have been developed to combine the flexibility, processability, toughness and durability properties of organic polymers with the abrasion resistance, hardness, chemical resistance, weatherability and UV-resistance of inorganic polymers [16].

2.2 Thermal barrier and flame retardant coatings

In this section, the coatings used for improving thermal barrier and fire resistance applications of varying material substrates are discussed.
2.2.1 Thermal barrier coatings

Thermal barrier coatings (TBCs) are usually applied to metallic surfaces of engine components operating at elevated temperatures, such as aircraft and rocket engines, industrial gas turbines, marine propulsion units, pistons and cylinders in diesel engines, in compressors and in chemical and petroleum plants, etc. The metals usually used in these applications vary from superalloys (various combinations of Fe, Ni, Co, and Cr), titanium alloys, niobium alloys and steel. The primary function of a TBC is to provide a low thermal conductivity barrier to heat transfer from the hot section in the engine to the surface of the coated metal component. By attaching a layer of ceramic particles, surface temperature of metallic component working at high temperatures can be reduced by 100-300 °C [17,18]. This temperature drop reduces the oxidation rate of the thermally activated metal substrate, and so delays failure by oxidation. It also retards the onset of thermally induced failure mechanisms (i.e. thermal fatigue), which contribute to extend the maintenance interval and component lifetime. Generally, TBC systems are comprised of three separate layers to achieve thermal barrier effectiveness [19], as illustrated in Figure 2.1.

![Figure 2.1: Illustration of coating construction of barrier layers and the roles of individual sub-layers](image)

The first layer is the bond coat and as the name implies, it bonds the coating to the substrate. The bond coat is usually a metallic layer made of a nano-structured ceramic-metallic composite, 75-125 μm thick [20]. Two types of materials used for bond coats are the NiCoCrAlY system or Pt-modified diffusion aluminide type [21]. This layer also helps in generating the second coating layer of thermally grown ceramic oxide, produced when the coating is subjected to a high temperature. The low pressure plasma spray (LPPS), vacuum plasma spraying (VPS) or high velocity oxygen fuel (HVOF) methods are typically used to apply the bond coat [22,23]. Nanoparticles of alumina oxide and nitrides
are usually added to the bond coat, which catalyse the thermal growth of the oxide layer. This thin (3-10 μm) thermally grown aluminium rich oxide layer’s role is to inhibit the oxidation of the bond coat. For the outer layer, the top coat is a thermally protective ceramic coating with a low thermal conductivity, which is required to maximize the thermal drop across the thickness of the coating [24]. A 100-375 μm thick layer of yttria-stabilized zirconia (YSZ) is the most preferred material for this function [19,20], due to its low thermal conductivity and its relatively high thermal expansion coefficient compared to many other ceramics. Pure zirconia exhibits an extremely low thermal conductivity, 1.5-2.0 W/mK [25]. Also, it has relatively high strength, wear resistance, and fracture toughness. However, zirconia also exhibits polymorphism as a function of temperature, primarily between the monoclinic, tetragonal, and cubic phases [26]. To avoid negative effects of phase changes of this ceramic at higher temperatures, such as micro-crack propagation through volume changes, it should be partially or fully stabilized with a stabilizer material, such as MgO, CaO, CeO₂ and Y₂O₃ oxides [27]. The most commonly used stabiliser for zirconia is yttria (Y₂O₃). From the literature, 6-8% yttria (Y₂O₃) contents in YSZ have been found to be best when deposited on gas turbine blades as a ceramic top coat [27,28]. Mostly, the YSZ layer can be fabricated either by the dry route or by the soft chemical process. The dry processes include atmosphere plasma spraying (APS) [29,30], electron beam physical vapour deposition [31], chemical vapour deposition [32]. For the chemical route, a sol–gel deposition is used [33].

Most of these techniques of application on a metallic substrate require very high temperatures, even in the sol-gel technique after dip coating the substrate in a solution (e.g. yttria stabilised zirconia slurry) the heat treatment is performed at 950 – 1150 °C [34], which is a seriously limiting factor for application onto the surface of fibre-reinforced polymer composite materials. Furthermore, the major drawback of TBCs is their brittleness, which makes them highly incompatible with ductile substrate materials such as polymer matrix composites.

2.2.2 Nanoparticulate coatings

Recently, nanocomposites have been explored for the development of flame retardant coatings, usually by the addition of nanoclay and nanosilica into the polymer coating formulation [35,36,37]. Compared to the traditional flame retardant coatings, obtained from
resin binders and flame retardant fillers/additives, nanocomposite coatings can combine the advantages of rigidity of the inorganic phase and softness of the organic phase more efficiently, or endow the coatings with new functionality resulting from nano-effects or synergistic effects [38]. The major concern within this kind of coatings is the dispersion of nanoparticles, due to the platelet structure and high aspect ratios of nanoclays and nanotubes. In nanocomposite coatings, the addition of nanoparticles such as nanoclay, nanosilica and carbon nanotubes impart flame retardancy by the migration of nanostructures onto the burning surfaces and formation of a protective char layer, which serves as a thermal barrier to slow down the release of volatile decomposition products and fuel release from the combustible substrate to the burning zone as illustrated in Figure 2.2.

![Figure 2.2: A mechanism of thermal barrier formation in nanocomposite coatings](image)

Alternatively, carbon nanofibres (CNF), single-walled carbon nanotubes (SWCNT) and multi-walled carbon nanotubes (MWCNT) have also been used to develop a thermal insulative sheet/mat, which can either reduce or block heat transmission through its layers. Zhao et al. have recently developed a novel technique of making carbon nanofibre (CNF) sheets and carbon nanotube (CNT) membranes to be used as surface insulative materials for glass fibre-reinforced polymeric composites by putting the membranes on the top of the glass fabric layers during composite preparation [39,40,41]. When exposed to fire, both the CNF/CNT and charred materials functioned as excellent insulators in improving the fire retardancy of the composite. A synergistic interaction between CNF/CNT and charred materials was also observed [42]. By incorporating clay in CNF sheet and CNT membrane, the fire retardancy performance of composites could be further improved [43,44]. It was observed that one single layer of these sheets/membranes was not enough to significantly improve the fire retardancy of the composite laminate and hence multilayers were used [45].
2.2.3 Flame retardant polymeric coatings

Flame retardant (FR) coatings have been designed for use as fire protection methods to interrupt or hinder the combustion processes of different substrates made from metal, wood, polymers and textile products when exposed to fire. The presence of a flame retardant coating delays or slows the time to ignition, time to flash over, smoke development, spread of flames, release of toxic gases, release of corrosive chemicals and the release of heat. These coatings interfere with the combustion of the underlying substrate at various stages of the process, e.g. during heating, decomposition, ignition or flame spread. There are two types of FR coatings: intumescent based or non-intumescent type [46].

2.2.3.1 Intumescent coatings

The intumescent coatings are used worldwide as “passive fire protection” materials that insulate substrate structures from the effects of the elevated temperatures that may be generated during a fire [47]. Intumescent coatings are available as solvent-based or water-based systems, which can be applied in an economical and simple way, such as by spray, brush or roller, onto several materials including metallic materials, polymers, textiles and wood. A typical intumescent system contains three main components [48].

1) A carbonisation agent (carbonific), which is carbon rich polyhydric compound that influences the amount of char formed and the rate of char formation.

2) An acid source, usually containing or generating poly (phosphoric acid) or other acid which promotes char formation.

3) A blowing agent, which decomposes and releases non-flammable gases (e.g. CO₂, H₂O and NH₃) that expands the char and forms a swollen multi-cellular layer, such as the melamine, which on heating releases NH₃.

After activation by fire or heat, a sequential chemical reaction between several chemical products takes place, which generally involves the decomposition of the acid source to generate a mineral acid, and then the acid reacts with the carbonisation agent to form the carbonaceous char, while the blowing agent generates the gases. The formed gases will expand the char. The swelling occurs due to the gases released following heating becoming trapped in the viscous fluid char layer and increasing the volume of the coating, and then a
multi-cellular char structure of low thermal conductivity voids (bubbles) is formed [49,50]. The expansion continues until the blowing agent is exhausted, or the solid matrix is insufficiently elastic. The solid matrix typically incorporates a polymer binder, which on heating promotes crosslinking reactions, and hardens the structure. The multi-cellular char structure is an efficient heat barrier acting as a physical barrier. This barrier can help in delaying ignition of the substrate; reducing the heat and mass (oxygen and pyrolysis products) transfer between the combustible substrate and the heat source; hindering propagation of the flame and eliminating a possible source of further flame propagation.

Another type of intumescent coating is one containing expandable graphite. The expandable graphite on heating expands and forms a thermally insulative layer on the surface of the substrate [51].

Although intumescent coatings can provide good thermal barrier performance, there are some disadvantages. For instance, the high loadings required to achieve the necessary level of performance leading to viscous paints and hence, altering the properties of the substrate. Also, the water soluble nature of water-based intumescent coating types will permit leaching, affecting the durability of those coatings.

2.2.3.2 Non-intumescent flame retardant coatings

In cases of a non-intumescent flame retardant coating, a popular way to impart flame retardancy is by mixing flame retardant (FR) additives in the coatings (i.e. paint or lacquer). Such a binder matrix may be composed of polyacrylates, polyurethanes, epoxy resins or vinyl resins. These coatings are designed such that they do not sustain combustion; they should not spread the flame by rapid combustion or contribute a significant amount of fuel to the fire. In the absence of a significant voluminous protection, however, such coating provides low temperature resistance to prevent rapid heat transfer through the substrate. Generally, there are several types of flame retardant additives: halogen-based; phosphorus-based; nitrogen-based; silicone-based and inorganic additive incorporated systems, used in FR coatings. FR additives function by different mechanisms as illustrated in the following discussion, but some of the more commonly applied materials will show several FR mechanisms which can vary with burning conditions.
Halogen-containing FR coatings

Halogenated flame retardant systems are widely used in FR coating formulations. Many halogenated-FR coating formulations have been used for various substrates, such as chlorinated alkyd coatings containing zinc borate [52] and PVC coating systems containing antimony trioxide or and zinc borate [53]. These halogenated-FR coatings interrupt the combustion process by forming halogen radicals, which remove free oxygen and hydroxyl radicals formed in the gas phase. Efficiency depends on the type of halogen (the effectiveness increases in the order F<Cl<Br<I), number of halogen atoms contained in the flame retardant (usually containing 50-85%) and the rate of halogen release. However, there are environmental concerns about their use as a large amount of smoke and toxic by-products such as hydrogen halides are produced during burning of halogenated systems.

Phosphorus-containing FR coatings

Phosphorus-containing FRs can exhibit both condensed phase and/or gas phase flame retardant action [54]. These FRs have been used in polymer coatings/films on varying substrates. For instance, ammonium polyphosphate (APP), allyldiphenyl phosphine oxide (ADPPO) and 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) are widely used in epoxy resin coating systems [55,56,57]. On heating, phosphoric acid is released which catalyses dehydration reactions of the resin leading to char formation. On further heating, phosphoric acid polymerises to polyphosphoric acid, which forms a viscous layer on the surface of the burning polymer. This serves as a physical barrier to heat transfer from the heat source to the substrate and to diffusion of gases. Although phosphorus-containing FRs are found to generate less toxic gases and smoke during combustion compared to other FRs, there are some critical arguments based on their potential environmental and health hazards, such as acidic erosion, eutrophication from hydroxylation of the phosphorus compounds, or even some potential carcinogenic activities [58].

Nitrogen-containing FR coatings

Nitrogen-containing FRs are considered as environmentally friendly and non-toxic flame retardant systems. Most nitrogen-containing FRs used in the coatings are based on melamine derivatives [59,60,61]. The nitrogen-containing FR coatings can provide several
functions, e.g. they form crosslinked molecular structures within the coating. In the vapour phase, they release non-flammable gases (i.e. ammonia or nitrogen with no increase in char formation), which results in delayed ignition time of the substrates. Moreover, these FRs also can work in synergy with phosphorus-containing FRs [58]. As a result phosphorus (P) and nitrogen (N)-containing compounds are the subject of increased interest and are used as phosphorus–nitrogen based coating systems [62,63,64].

*Silicon-based FR coatings*

Silicon-containing FRs show very promising properties compared to halogenated FRs because they are more environmentally friendly. They function mainly in condensed phase, forming a thermally insulative silicate barrier layer on the surface of the burning polymer, which can hinder the supply of oxygen and heat to the polymer and diffusion of combustible volatiles from the polymer to the burning zone. Some silicates can release silicic acid, which catalyses the char formation of the polymer. They however, do not release toxic gaseous and corrosive smoke during combustion like halogenated flame retardants [65,66]. The preparation of silicon-based coatings mainly involves the incorporation of silicones, silicates, organosilanes or silsesquioxanes as fillers or copolymer or as the main polymer matrix in the coating system. Silicon-based coatings, such as silicone containing epoxy coatings, are able to resist temperatures of up to 800-1000 °C [67,68].

*Inorganic additives incorporated FR coatings*

Inorganic additives, such as metal hydroxides or boron compounds, interrupt the burning process by physical processes, such as releasing large volumes of water of hydration or non-inflammable gases, absorbing heat due to decomposition or by producing a non-flammable surface layer [69]. These inorganic additives may be used as synergistic co-additives or main FR elements within the coating. For example, aluminium hydroxide (ATH) and magnesium hydroxide are used in thermosetting polymer coating formulations (polyurethane based and epoxy based). It is claimed that a metal hydroxide concentration of around 30 wt% in the coating matrix provides self-extinguishing character to the substrate [70]. This indicates that these FR coating systems require high loadings (> 30 wt%) to achieve the desired level of fire retardance, this may affect the physical properties of the coating and the substrate.
Study of the literature indicates that there has been previous work upon the application of FR coatings on fibre-reinforced polymer composites [71,72,73], which has already been discussed in Chapter 1.

2.3 Techniques of surface coating application on polymeric substrates

The application methods and conditions of film formation play important roles in determining the ending properties of the coating. The methods adopted depend on the type of coating system being used and the nature of the surface. For metal and ceramic coatings, there are several coating processes, some examples being electroplating [74], electroless-plating (e.g. hot dipping, metal spraying) [75], electrogalvanising, PVD (physical vapour deposition), CVD (chemical vapour deposition) [76] and plasma spraying [77]. These are all high temperature processes. These techniques are suitable for substrates that can sustain temperature higher than 600 °C, such as metallic substrates. The application of these coatings on polymer substrates is extremely limited due to the low thermal stability of organic compound. The coating application techniques for polymers in general require heat processing at temperatures below the glass transition (T_g) and decomposition temperatures of the polymer component. Epoxy resins typically start softening at 120 – 180 °C and decompose around 250-300 °C depending on the type of resin; thus coatings are usually applied to the polymer substrates at lower temperatures by means of non-thermal application techniques. Some techniques suitable for polymeric substrates are discussed below.

2.3.1 Paint brush, spraying and roller techniques

The most widely used methods of applying surface coatings are spreading methods (e.g. brush application, roller application), spraying methods (e.g. conventional spray, air spray) and flow coating methods (e.g. dipping, K-bar coater). These methods are low temperature processes and possibly operated under ambient conditions. They also provide a simple but effective means of applying paints, printing inks, lacquers and other solvent/water borne surface coatings onto many types of substrate including paper, plastics, metal plates, glass plates, wood, etc. The advantages and disadvantages of these methods are briefly discussed below.
2.3.1.1 Paint brush application

Paint brush application is always undertaken using an appropriately sized, good quality synthetic or natural fibre brush compatible with the product being applied. This application technique is relatively slow and is particularly suitable for the application of stripe coats and for coating complex areas. Limitations of brush application are that it may not produce a uniform coating thickness. This method is not practical for large surfaces and it may leave unsightly brush marks with coatings that do not level well.

2.3.1.2 Roller application

Roller application is faster than brush for large area coating, but this does not work the coating into surface irregularities as well as brushes. The roller should be charged uniformly with the coating, rolled over the surface with reasonable pressure and moved in all directions to distribute the coating evenly. However, control of film thickness is not easily achieved by this application method.

2.3.1.3 Spray application

This treatment is a widely accepted and rapid method of coating application. The basic principle of spray application is to atomise the coating into a fine spray by a low-pressure air stream and to direct the spray onto the object to be coated. The coating is contained in a closed container and transferred to the gun head by means of filtered compressed air. The spray gun is connected to a source of compressed air and utilises high-pressure air to atomise the paint and direct it onto the surface to be coated. This high-pressure air promotes overspray and blow back. However, this spray coating requires a certain amount of skill and experience. If conventional spray application is not controlled correctly, large losses of coating can result from overspray and rebound from the surface. The other major disadvantage of this application is that high build coatings cannot generally be applied by this method, as most coatings have to be thinned to a suitable viscosity for satisfactory atomisation, and so lose their high build properties.

2.3.1.4 K-bar coater application [78]

A K-bar coater is widely used for the application of paints, varnishes and other liquid surface coatings to produce quick, accurate and repeatable samples, usually only for experimental and developmental investigation purposes. Wired K-bars are produced by
winding precision drawn stainless steel wire onto a stainless steel rod resulting in a pattern of identically shaped grooves, as shown in Figure 2.3. These grooves precisely control the wet coating thickness. Close wound bars will produce coating thickness from 4 to 120 μm. Higher coating weights up to 500 μm can be obtained using spirally wound bars. These K-bars can firmly spread the wet coating over the surface with uniform and controllable thickness as illustrated in Figure 2.3.

Figure 2.3: Standard K-bar types and application procedure [78]

Figure 2.4: Various stages in the process of film formation of particles dispersed in a solvent system of a polymer coating
Once the liquid surface coating has been applied, the principal mechanisms by which the binders form films consists of three basic steps [79]: (1) the reaction with oxygen from the air (oxidation) after the coating has been applied by the selected technique; (2) evaporation of the solvent and/or water trapped in the coating from the carrier (solvent evaporation) accompanied by the polymer ordering/deformation and (3) chemical crosslinking (curing or polymerisation) to form a thin film either by conventional thermal curing through the use of thermal ovens, infrared or radiation curing processes, electron beam systems, laser, UV curing and plasma polymerisation [80]. The procedure of the formation of a polymer film coating containing solid particles under thermal curing conditions is illustrated in Figure 2.4.

2.3.2 Non-thermal plasma

In general, the plasma is a partially or fully ionized gas which consists of a multitude of species such as radicals, positive and negative ions, metastables, electrons, excited molecules or atoms and photons (UV and visible) [81]. Plasmas occur over a wide range of temperatures (e.g. low or high temperature plasmas) and pressures (e.g. low, atmospheric or high pressure). In laboratories plasma is generated by coupling energy to a gaseous medium through thermal energy or by applying a voltage or by injecting electromagnetic radiation [82]. In terms of electron density and temperature, plasmas are generally divided into two main groups: thermal plasmas also known as equilibrium plasmas, and cold plasmas or non-equilibrium or non-thermal plasmas. The typical classification of different kinds of plasma and an overview of the main characteristics is presented in Table 2.1.

Table 2.1: Plasma classification [81,82]

<table>
<thead>
<tr>
<th>Plasma</th>
<th>Characteristics</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermal plasma</td>
<td>$T_e \approx T_{\text{ion}} \approx T_{\text{gas}} = 10^6$ - $10^8$ K</td>
</tr>
<tr>
<td>(Equilibrium plasma)</td>
<td>Electron density: $\geq 10^{20}$ m$^{-3}$</td>
</tr>
<tr>
<td>Non-thermal plasma</td>
<td>$T_e &gt;&gt; T_{\text{ion}}$</td>
</tr>
<tr>
<td>(Non-equilibrium plasma)</td>
<td>$T_e \leq 10^3$ K ($\approx 10$ eV)</td>
</tr>
<tr>
<td></td>
<td>$T_{\text{ion}} \approx T_{\text{gas}} \approx 300 - 10^3$ K</td>
</tr>
<tr>
<td></td>
<td>Electron density: $&lt; 10^{19}$ m$^{-3}$</td>
</tr>
</tbody>
</table>

Note: $T_e$: electron temperature, $T_{\text{ion}}$: ion temperature, $T_{\text{gas}}$: gas temperature
Based on Table 2.1, species produced in thermal plasmas are in thermal equilibrium, and hence electrons and ions have high temperatures. In contrast, the ion and neutral gas species in non-thermal plasmas have low energies, while the electrons have relatively high energies [83]. Hence, species produced in non-thermal plasma are not in a thermodynamic equilibrium and the temperature of the gas is usually below 150 °C. Therefore, thermally sensitive organic compounds or substrates are not damaged by these plasmas.

To generate and sustain non-thermal plasmas, the input of electrical power is necessary for dissociation and excitation of atoms and molecules with subsequent production of radicals and metastable molecular states. This is achieved by various electric power sources operating under a very wide range of conditions, for example alternating current (AC) or direct current (DC), low frequency (~50 kHz) or high frequency including radio frequency (RF) and microwave (~2.45 GHz) [84]. These plasma processes can be operated in a closed evacuated chamber under vacuum conditions (low-pressure plasma) or in an open system under atmospheric conditions (atmospheric pressure plasma). See Figure 2.5.

![Diagram of plasma discharge](image)

**Figure 2.5:** (a) Atmospheric pressure plasma and (b) Low pressure plasma

In coating applications on polymer substrates, non-thermal plasma can be utilized in the polymerisation of organic monomers in the vapour, liquid, and solid phases. This is a technique that employs high energy electrons present in glow discharges (plasma) to dissociate, ionise and fragment organic vapour molecules, thereby forming chemically reactive species, which polymerise on a surface to form a film coating [85]. Upon relaxing to their ground state the electrons emit UV and visible radiations in the plasma. All the
active species (e.g. radicals, ions, various neutral particles, and photons) have sufficient energy to break carbon-carbon and carbon-hydrogen bonds in the polymer as seen in Table 2.2.

<table>
<thead>
<tr>
<th>Glow discharge</th>
<th>Energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electrons</td>
<td>0-20</td>
</tr>
<tr>
<td>Ions</td>
<td>0-2</td>
</tr>
<tr>
<td>Metastables</td>
<td>0-20</td>
</tr>
<tr>
<td>UV/Visible</td>
<td>3-40</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Bond</th>
<th>Energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H—H</td>
<td>4.5</td>
</tr>
<tr>
<td>C—H</td>
<td>4.3</td>
</tr>
<tr>
<td>C—C</td>
<td>3.6</td>
</tr>
<tr>
<td>C = O</td>
<td>8.0</td>
</tr>
<tr>
<td>C = C</td>
<td>6.1</td>
</tr>
<tr>
<td>C ≡ C</td>
<td>8.4</td>
</tr>
</tbody>
</table>

Table 2.2: Energies available in a plasma and some typical bond energies [86].

There are three types of polymerisation reactions that can be induced by non-thermal plasmas techniques.

1) Plasma-state polymerization [87]: the polymerisation occurs only when polymerisable monomer vapours are introduced into a plasma. The polymer films formed by this method are significantly different from conventional polymers, due to the fragmentation of monomer molecules, followed by recombination of the fragments and deposition. Consequently, the mechanism of polymerisation by which an organic vapour polymerises under plasma is quite complex and can not be specifically described for the general case.

2) Plasma-induced polymerisation [88]: the polymerisation occurs when a plasma of an inert gas or an organic vapour (without addition of plasma gas) is created on the surface of liquid or solid monomers, previously applied to the polymer substrates. These monomers must contain polymerisable functions, such as double bonds, triple bonds or cyclic structures. Subsequently, a transfer of some active species from the plasma to the monomer takes place, and then the propagation of polymer chains occurs in bulk via a conventional polymerisation mechanism.

3) Plasma grafting [89]: the polymerisation occurs when a polymer substrate surface is treated with an inert gas plasma and the surface is left rich with free radicals. This surface is then exposed to an unsaturated compound without additional plasma
activation. The substrate reacts (couples) with the free radicals on the polymer and grafting occurs.

### 2.3.3 Ultraviolet (UV) curing technique

Ultraviolet (UV)-curing techniques are being increasingly used in coating applications due to advantageous characteristics such as rapid curing, low temperature requirement (or room temperature processes), reduced environmental pollution, high chemical stability, and low volatile organic compounds (VOC) emission [90]. To employ UV curable systems, the coatings should contain reactive chemical groups, which are linked together after energy-rich radiation (UV-radiation) has been applied onto the coating. This process can be started and maintained at ambient condition by radicals from an added photo-initiator. Usually 2–3 wt% of photo-initiator in the coating formulation is a reasonable starting point. After that the activated photo-initiator reacts with the monomers or oligomers and enables chain growth of the polymer network via photo-polymerisation. However, this curing process can be interfered with by oxygen inhibition as free radicals driving the reaction (e.g. activated photo-initiator radicals and growing chains) are scavenged by oxygen on the surface and in the upper layers of the coating. This leads to the formation of short chain segments, resulting in tacky surface layers and poor mechanical and physical properties of the coatings [91]. Generally, two main types of photo-initiator are used in UV curable coatings, which are:

- radical photo-initiators: free radicals are produced by UV radiation.
- cationic photo-initiators: protons or a Lewis acid can be produced by UV radiation.

<table>
<thead>
<tr>
<th>UV type</th>
<th>Wavelength (nm)</th>
<th>Energy per photon (eV)</th>
<th>Radiation sources</th>
</tr>
</thead>
<tbody>
<tr>
<td>UV-A (Long wavelength)</td>
<td>315 - 400</td>
<td>3.10 – 3.94</td>
<td>Black light</td>
</tr>
<tr>
<td>UV-B (Medium wavelength)</td>
<td>280 - 315</td>
<td>3.94 – 4.43</td>
<td>Metal halide or mercury vapour lamps</td>
</tr>
<tr>
<td>UV-C (Short wavelength)</td>
<td>200 - 280</td>
<td>4.43 – 12.4</td>
<td></td>
</tr>
<tr>
<td>Vacuum UV</td>
<td>100 - 200</td>
<td>6.20 – 124</td>
<td>Xenon-excimer source lamp</td>
</tr>
</tbody>
</table>
It must be noted that a suitable UV-radiation energy wavelength is essential to initiate the curing process in addition to the reactive photo-initiator. UV-radiation energy waves have wavelengths over the range 100 to 400 nm (between X-rays and visible light spectra). The division of UV radiation may be classified as illustrated in Table 2.3. In terms of curable effects, photo-initiators developed for curing of coatings containing pigments, additives or filler typically have higher molar extinction coefficients in the longer wavelengths region from 300 nm to 450 nm than those used for curing clear coating formulations. Longer wavelength light is also essential to provide an all through cure required with thicker coatings [93]. Based on these advantageous characteristics, UV cure techniques are highly attractive for FR coating applications on heat sensitive substrates. Such coatings can be made by adding the appropriate FR elements (e.g. boron, phosphorus, silicone) into UV-curable coating binders or by polymerisation of FR monomers using UV-curable systems [94,95].

2.3.4 Graft polymerisation techniques

Currently, interest is being shown in an alternative coating application for FR coatings. This is grafting of FR compounds or FR monomers onto the surface of the polymer or natural fabric substrates. Phosphorus-containing monomers or compounds are usually employed for this application [96,97]. The typical technique of graft polymerisation is a radical polymerisation of various monomers achieved by various surface grafting methods such as chemically induced-, UV-induced- [98], gamma irradiation-induced- [99], and plasma-induced-grafting [100]. These techniques permit covalent grafting of small functional groups and macromolecular compounds onto the surface of polymeric materials.

![Figure 2.6: Graft polymerisation of FR monomers on polymer substrate](image-url)
The principle of this approach is to apply the monomers on the substrate, induce grafting polymerisation of these monomers via UV light or plasma activation and then polymerisation occurs on the substrate with structure retention of the monomer. The scheme for a graft polymerisation is shown in Figure 2.6. For grafting techniques, chemical or photo-initiators are required to start the polymerisation. Usually, the initiator is a very reactive species which is activated by light or temperature changes or by another reactive chemical added to the solution. Depending on the type of activation, the reaction can be free radical, living anionic, or living cationic surface reactions. In free radical polymerisation, three reaction steps have to be considered, regardless of their occurrence in solution or at a surface [101]. At the onset, the initiator molecules have to be immobilized at the solid surface and at which point polymerisation has been initiated. After surface immobilization the activation leads to a radical, or a positively or a negatively charged initiator group. By reaction with a FR monomer, the activated site is transferred to the monomer, which itself reacts with another monomer. Additionally, radical reactions promote side-reactions as crosslinking or a combination between polymer chains, leading to a higher polydispersity. This chain growth is terminated if all of the monomers are used or side-reactions, especially for radical polymerisation, stop the reaction.

2.3.5 Layer-by-layer (LbL) assembly

Layer-by-layer (LbL) assembly is a highly tailorable coating technique capable of creating thin and multilayer coatings from water or solvent-based formulations. This technique has been used as a simple, highly inexpensive as well as environmentally friendly coating application method for polymeric material substrates, such as textiles, membranes or foams (polyester, polyamide and polyurethane) [102,103,104]. LbL films are typically created by alternate adsorption of materials through complementary interactions [105]. This is illustrated in Figure 2.7 where a substrate is exposed to polyelectrolyte solutions or suspensions of positively and negatively charged species where the assembly is driven by electrostatic interactions [106]. In this case, the deposition is repeated until the desired number of bilayer (or cationic-anionic pairs of layers) is achieved. The thickness of each individual layer may be ranking from 1 to more than 100 nm, depending on chemistry, molecular weight, charge density, temperature, deposition time, counterion and pH of species being deposited.
The ability to control coating thickness down to the nano-level, to easily insert variable thin layers without altering the process, to avoid disturbing intrinsic mechanical behavior of the substrate, and to process under ambient conditions are some of the key advantages of this deposition technique [106,107]. Furthermore, altering the order and composition of layers provides limitless opportunity for new functionality to be deposited onto the next layer. Apart from electrostatic interactions, the multilayer film deposits can be built up also through donor/acceptor interactions, hydrogen bonding, and covalent bonds [102,108]. The LbL assembly has been adapted to prepare coatings of a wide range of materials including polymers, bio-macromolecules, FR additives, nanoparticles and carbon nanotubes [103-107]. The deposition protocols for LbL assembly techniques can be made by a simple dipping or more advanced techniques, which include spin-coating [109], spray assembly [110] and roll-to-roll processes [111].

### 2.4 Adhesion of polymeric coatings

After application, a strong adhesion between coating and substrate is desirable. Adhesion is defined as the state in which two different materials are held together at their surfaces by physical or chemical valence forces, or both, such that it is necessary to do work to separate them [112]. The most critical issue in creating a very strong adhesion is the formation of a continuous film on top of the surface, which is able to cover the surface of the substrate and create an integral solid film. Some examples of various mechanisms that can lead to adhesion during adhesive bonding between a polymer coating and a certain substrate are illustrated in Figure 2.8.
Figure 2.8: Possible adhesion phenomena between a coating and a certain substrate

For mechanically interlocked interfaces (Figure 2.8 (a)), the good adhesion of this interlocking effect occurs only when an adhesive penetrates into the pores, holes and crevices and other irregularities of the film/substrate interface, and locks mechanically to the substrate [113]. The adhesive must not only wet the substrate, but also have the right rheological properties to penetrate pores and openings in a reasonable time. In Figure 2.8 (b and c), chemical bonding, the adhesion occurs via the chemical bonds formed across the adhesive/substrate interface. The chemical bonds are generally considered as primary bond interactions, such as ionic and covalent bonds, and secondary force interactions (physical interactions), such as van der Waals interactions. These bonds can greatly participate in the level of adhesion between both materials. The typical strength of a covalent bond is in the order of 100 to 1000 kJ/mol, whereas those of van der Waals interactions do not exceed 5 kJ/mol [114]. The electrostatic interaction in Figure 2.8 (d) can create adhesion by the difference in electronegativities of adherent materials. Adhesive force is attributed to the transfer of electrons across the interface creating positive and negative charges that attract one another. For polymer diffusion interfaces (Figure 2.8 (e)), the polymer chains from the substrate and from the coating can diffuse into each other layer by inter-penetration of macromolecules across the interface, thus creating an interphase [115].

2.5 Characterisation of coatings and films

Because of the wide range of coating characterisation techniques, the discussion in this section is limited to the methods of particular interest to the current studies. These are the
measurement of the thickness of films on substrates, adhesion between the coating/substrate, the surface morphology of coated samples and the water resistance of coatings. The thermal barrier and fire testing are also discussed in this section.

2.5.1 Measurement of dried coating film thickness

The ASTM D1005 test method is particularly applicable to the measurement of free films and is also satisfactory for the measurement of films on laboratory test panels. This test method covers the measurement of film thickness of dried films of paint, varnish, lacquer, and related products using micrometers [116]. This method has four different procedures.

- A: Stationary micrometer for measuring coatings applied to plain rigid surfaces.
- B: Stationary micrometer for measuring free films.
- C: Hand-held micrometer for measuring coatings applied to plain rigid surfaces.
- D: Hand-held micrometer for measuring free films.

Procedures A and B utilize stationary micrometers and procedures C and D, hand-held micrometers. Procedures A and C are not recommended for films less than 12.5 μm in thickness. The minimum thickness required for Procedures B and D is a function of that required to enable removal of the sample as a free film. The accuracy and precision of the thickness measurements may be influenced by the deformability of the coating. This test method is not applicable to coatings that are readily deformable under the load of the measuring instrument. The accuracy and precision of the thickness measurements are also influenced by the uniformity of the substrate when the coatings are applied to laboratory test panels.

2.5.2 Surface characterisation

Several surface characterisation methods, which are used in this work, will be introduced in detail here.

*Scanning electron microscopy (SEM)*

Among many surface characterisation methods for surface coatings, scanning electron microscopy (SEM) is one of most common for characterisation of polymer coating films.
In SEM both surfaces and cross-sections of coatings can be studied. The SEM method uses a high-energy electron beam to emit electrons from the surface of the sample of interest. The electron beam, with energy ranging from a few hundred eV to 20 k eV, is focused by condenser lenses and can be moved in the x and y axes directions by scanning coils or deflection plates. The spot size of the electron beam is typically of 0.4 nm to 5 nm in size, and the resolution of SEM is approximately 1 nm to 20 nm [117].

_Infrared attenuated total reflection spectroscopy (IR-ATR)_

Infrared attenuated total reflection spectroscopy (IR-ATR) is a non-destructive method to probe the chemical composition of liquid coatings or solid film samples. IR spectroscopy allows identification of the coating and/or film sample's chemical composition or the presence of different chemical functional groups, which are detected as absorbed radiation or percent transmittance at specific frequencies.

![Diagram of IR-ATR setup](image)

**Figure 2.9: IR-ATR setup to identify chemical characteristics of the coating on a substrate**

The IR-ATR setup for coating/film characteristics is illustrated in Figure 2.9. IR radiation is focused onto the end of the internal reflection element (IRE), which can be either crystal or diamond, and then reflects across the length of the IRE. The IR radiation is guided in IRE material with a high refractive index (>2.4 to 4), for example diamond. The attenuated total reflection at the interface of the sample and the diamond produces an evanescent field which penetrates into the sample by 0.5 to 3.0 μm. The IR radiation is guided back into the spectrometer and onto the detector. After application onto a substrate, the coating is pressed on the IRE to ensure contact to the evanescent IR field [118]. By applying the coating/film directly onto the IRE, changes with time can be observed. The evaporation of solvents, and curing reactions can also possibly be investigated by this technique [119]. In addition, IR-ATR only characterises the surface of coating, but cannot give any information referring to chemical function or bonding of the interface between coating and substrate.
Surface wettability

Many plastics and thermosetting resins that have been used in surface coatings are hydrophobic, and are not naturally wettable. As a result of this character, the wettability (ability of a fluid to cover a surface) of a surface coating is an important property to determine as this will help to identify the end properties of the coating. ASTM D7334 – 08 is a standard that is useful for characterising the wettability of polymer coating surfaces [120]. A surface that is easy to wet indicates a coating that is more likely to give good adhesion and appearance, and suffer minimally from surface tension related defects (i.e. cratering, pinholing and orange peel) by comparison with the behaviour of non-wettable surfaces. Based on this standard, an organic liquid such as a solvent or water can be used as a test liquid to characterise the wettability of a substrate or coating surface via the advancing contact angle. A low advancing contact angle value (<45°) is indicative of wetting and angles of 10 to 20° are indicative of excellent wetting. The resultant contact angle will depend on the surface tensions of the test liquid and the test surface, for instance a low surface tension (energy) test surface will not be wet by a high surface tension liquid. In this case, the contact angle is defined as the angle formed by the intersection of the liquid-solid interface and the liquid-vapour interface (geometrically acquired by applying a tangent line from the contact point along the liquid-vapour interface in the droplet profile) [121].

![Figure 2.10: Illustration of contact angles formed by liquid drops on a smooth homogeneous solid surface [122]](image)

Ideally, the shape of a liquid droplet is determined by the surface tension of the liquid. As described in Young’s equation [123], the contact angle of a liquid drop on an ideal solid surface is defined by the mechanical equilibrium of the drop under the action of three interfacial tensions (γlv, γsv, and γsl) as seen in Figure 2.10. γlv, γsv, and γsl represent the
liquid-vapour, solid-vapour, and solid-liquid interfacial tensions, respectively, and $\theta$ is the contact angle. In the first case, the wetted surface is energetically more favourable than the “dry” surface ($\gamma_{sv} > \gamma_{sl}$). The resulting contact angle will be smaller than 90°, indicating that the surface has high wettability. If the liquid was water, the solid surface is considered to be hydrophilic. In the second case, $\gamma_{sv} < \gamma_{sl}$, the interfacial tension of the wetted surface is higher than the interfacial tension of the solid surface in contact with the vapour phase. The resulting contact angle will be larger than 90°, which generally means that the surface is low wettability, so the liquid will minimize its contact with the surface and form a compact liquid droplet. If the liquid was water, the solid surface is considered to be hydrophobic. In cases of complete wetting, it will occur when the contact angle is 0°, as the droplet turns into a flat puddle, while super-hydrophobic surfaces, water contact angles are usually greater than 150°, showing almost no contact between the liquid drop and the surface [122]. Although the contact angle is governed by the surface tensions of the test liquid and test surface, the angle cannot provide a surface tension value directly.

2.5.3 Adhesion of coatings

The durability of coatings is of prime importance in many applications and one of the main factors that govern this durability is adhesion. A variety of recognised methods can be used to determine if a coating is bonded to the substrate. Typically, the cross-cut (or tape-pull test) and the pull-off method are used to determine adhesion specifications. After any test it is important to record if the bond failure was adhesive (failure at the coating / substrate interface) or cohesive (failure within the coating film or the substrate). A cross-cut test is performed in accordance with ASTM D3359-08 [124] and BS EN ISO 2409:2007 [125].

<table>
<thead>
<tr>
<th>Appearance</th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>0%</td>
<td>&lt; 5%</td>
<td>&lt; 15%</td>
<td>&lt; 35%</td>
<td>&lt; 65%</td>
<td></td>
</tr>
</tbody>
</table>

Table 2.4: Principle of classifying film adhesion in the cross-cut test [125]
To perform the test, a pressure sensitive tape is applied and removed over cuts made on the coated material surface. Usually 6 cuts are produced in parallel with a distance of 1 to 2 mm between each a similar 6 sets of cuts are performed perpendicular and crossing the first six cuts (see Table 2.4). Afterwards an adhesive tape is pasted over the pattern and removed with a particular force. The classification of the adhesion is based on estimating the area where the coating has been removed by this procedure. The classification protocol is also shown in Table 2.4. Class 5 indicates perfect adhesion, classifications 4 and 3 indicate partial decohesion, whereas classifications 2 and 1 indicate poor adhesion to the substrate. Alternatively, a more quantitative test for adhesion is the pull-off test where a stud is glued with the coating and is subject to axial tension until detachment of the film occurs. The result is the maximum tensile stress that is possible at the interface. Additionally, also a torque can be applied about the axis of the stud, and thus, the process of detachment reveals the maximum shear stress. A standard method for the application and performance of this test is available in ASTM D4541 and ISO 4624 [126].

2.5.4 Water resistance of coatings

Immersion in water can cause the degradation of coatings. The investigation of how well a coating resists water immersion is helpful in predicting the coating service life. Failure in a water immersion test may be caused by a number of factors including a deficiency in the coating itself, contamination of the substrate, or inadequate surface preparation. The ASTM D870-02 [127] and BS EN ISO 2812-2 [128] standards cover the basic principles and operating procedures for testing water resistance of coatings by the partial or complete immersion of coated specimens in distilled or de-mineralized water at ambient or elevated temperatures. The apparatus for the test is relatively inexpensive and can be as simple as a glass beaker for small scale coated samples, or it is possible to use very large tanks for testing coated pipe or other large coated samples. The test detail is limited to the methods of obtaining, measuring, and controlling the conditions and procedures of these water immersion tests. It does not specify specimen preparation, specific test conditions, or evaluation of results. Typically, the results for these tests are reported in a pass or fail determination, but the degree of failure may also be measured. A coating system is considered to pass if there is no evidence of water-related failure after a specified period of time at elevated temperature. It should be noted that results obtained from water immersion tests in accordance with these two standards should not be represented as being equivalent.
to a period of exposure to water in the natural environment, until the degree of quantitative correlation has been established for the coating or coating system.

2.5.5 Thermal barrier and fire testing methods

In order to evaluate the fire performance of coatings in fire scenarios, several thermal barrier and fire test methods have been employed. ASTM D1360-98 is a standard method that is used to determine, quantitatively, the fire retardant properties of a coating or coating system on a wood surface [129]. This method provides good assessment under specified conditions, which measures combustibility through mass loss and char index. However, it does not purport to address all of the safety concerns (i.e. fire hazard of materials) under actual fire conditions. Alternatively, BS 476 Part 6 standard can be used to determine the fire propagation of the coating on building materials and structures, such as internal wall and ceiling lining materials [130], or BS 476 Part 7 standard that can determine the classification of the surface spread of flame of coated products [131]. In addition, there are several test methods that have been developed to assess the heat insulation performance of an intumescent coating on structural steel. For instance, UL 1709 is a recommended standard test to evaluate the fireproofing systems for petrochemical processing plant [132]. UL 1709 simulates hydrocarbon rapid temperature rise pool fire conditions. It subjects an intumescent coated steel column to a heat flux that produces a temperature of 2000°F (1093°C) in 5 minutes, while thermocouples are attached to the reverse of the steel plate allowing measurement of temperature versus time (UL1709 curve). After that time, the furnace temperature is held constant for the remainder of the test, subjecting the test fireproofing system assembly to a heat flux of 65,000 BTU/ft²-hr. However, limitations of this method include a failure to correlate with the large-scale flame spread results and also very limited applicability to highly flammable substrates. Hence, many researchers have modified this test by changing sample size, size of furnace and heat flux used in the furnace to get data similar to that in the standard [133,134,135]. Apart from these test methods, the cone calorimeter is widely accepted as the best bench-scale method for determining the flammability of coated materials [133,136]. It will be discussed in more detail in Chapter 3.
2.6 References


[40] Z. Zhao and J. Gou, “Improved fire retardancy of thermoset composites modified with carbon nanofibers”, Science and Technology of Advanced Materials, 10, pp. 6 (2009)


Chapter 3

EXPERIMENTAL

This chapter discusses the experimental methodology developed to surface treat glass fibre-reinforced epoxy (GRE) composite samples with four types of coatings. The coating types include (i) intumescent based (ii) nanoclays (iii) ceramic particles and (iv) chemical coatings by polymerising monomers on the surface. Firstly, the materials used for GRE composite and preparation methodology are discussed. This is followed by materials for each coating type and its method of application on GRE composite laminate surfaces. Then the testing protocols used for evaluating the effects of coatings on physical, thermal and mechanical properties of GRE laminates are discussed.

3.1 Glass fibre-reinforced epoxy (GRE) composite

3.1.1 Materials

3.1.1.1 Epoxy resin system [1]:

- Epoxide resin: Araldite LY 5052 (Huntsman) containing an epoxide phenol novolac resin (60-72 wt%) and butanedioldiglycidyl ether (34-42 wt%).
- Hardener: Aradur CH 5052 (Huntsman) containing isophorone diamine (30-42 wt%), 2,2-dimethyl-4,4 methylenebis (cyclohexylamine) (50-56 wt%), and 2,4,6-tris (dimethylaminomethyl) phenol (1-7 wt%).

3.1.1.2 Glass fibre:

Woven roving glass fibre of E-glass type (290-300g/m², Glasplies)
3.1.2 Glass fibre-reinforced epoxy (GRE) composite preparation

Eight pieces of 300 mm x 300 mm woven E-glass fabric were used for each sample with the ratio of 50 wt% glass fibre and 50 wt% resin matrix. Firstly, the resin matrix was prepared by mixing Araldite LY5052 resin and Aradur CH 5052 hardener (30 wt% w.r.t epoxy formulation), and stirring with a glass rod until the mixture became homogenous. The glass/epoxy laminates were then prepared by a hand lay-up method. Using a roller, the first layer of glass fabric was impregnated with the epoxy resin mixture, another layer stacked on it and impregnated with resin. The process was repeated until eight layers were stacked together. After that the consolidated laminate was vacuum bagged and cured at room temperature for 12 h followed by a post cure at 80 °C for another 8 h. A pressure of 1 bar was applied to the laminate during the curing process.

![Diagram of GRE composite laminate fabrication](image)

**Figure 3.1:** The process of GRE composite laminate fabrication by hand lay-up and vacuum bagging techniques

After the GRE composite laminated was produced, the master GRE laminate was then cut into plaques of sizes suitable for different tests. These plaques were then independently coated by different coatings as discussed in following sections.
3.2 Intumescent Coatings

3.2.1 Materials

3.2.1.1 Epoxy based intumescent coating (M90) [2]: Firetex M90 (Leighs’ Paints) formulation is comprised of two component materials.

- Firetex DP1599 base resin containing an epoxy resin (10-25 wt%), ethyl hexyl glycidyl ether (2.5–10 wt%) and bisphenol F-epichlorohydrin (10–25 wt%)
- M90 hardener containing 2,4,6-tris (dimethylaminomethyl) phenol (2.5–10 wt%) and triethylenetetramine (2.5–10 wt%).

The intumescent chemicals composition, due to commercial sensitivity, is not given here.

3.2.1.2 Flame retarded epoxy based intumescent coatings (M93) [3]: Firetex M93 (Leighs’ Paints) formulation is comprised of two component materials.

- Firetex DP1600 base resin containing an epoxy base resin (10 – 25 wt%), DOPO (9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide) modified epoxy resin complex (10-25 wt%), 1,4-bis (2,3-epoxypropoxy) butane (10-25 wt%) and triphenyl phosphate (<1wt%)
- M93 hardener containing, zinc borate (<1 wt%), tetraethylpentamine (2.5-10 wt%) and 3-aminopropyltriethoxysilane (<2.5 wt%).

The intumescent chemicals are the same as in M90 coating.

3.2.1.3 Water based intumescent coating (FX5002) [4]: Firetex FX5002 (Leighs’ Paints) is a single component material, containing a vinyl acetate/vinyl ester copolymer system, thermally active pigments, water and butyl diglycol acetate. Intumescent chemicals due to commercial sensitivity are not mentioned.

3.2.2 Application of intumescent coatings on the GRE composite laminate

GRE laminates of 75 x 75 mm size and ~ 3 mm thicknesses were individually coated with three intumescent coatings to obtain 1, 3 and 5 mm coating thicknesses. The surface of GRE laminate samples was firstly cleaned with acetone, wiped very gently with a tissue and dried at room temperature for 10 min before applying any surface coating. The GRE laminates were weighed before and after coating. The coating process initially involved preparation of different intumescent coatings formulations, M90, M93 and
FX5002 (as described in Section 3.2.2), according to the manufacturer’s instructions and then each intumescent coating was independently applied on the GRE composite laminates’ surfaces by using a paint brush and a roller to get a uniform thickness. The thickness and mass of each of the coatings M90, M93 and FX5002 on GRE laminates are given in Table 3.1. After coating the laminate’s surface, the coated laminates were cured at room temperature for 24 h, and then post-cured at 80 °C for 4 h in an oven.

Table 3.1: Details of different coatings on the laminates (size 75 mm x 75 mm)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Coating thickness(mm)</th>
<th>Coating mass used for laminate (g)</th>
<th>Coating formulations (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GRE-M90 and GRE-M93</td>
<td>1</td>
<td>6.5</td>
<td>4.55 base resin/1.95 hardener</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>15.5</td>
<td>10.85 base resin/4.65 hardener</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>27</td>
<td>18.90 base resin/8.10 hardener</td>
</tr>
<tr>
<td>GRE-FX5002</td>
<td>1</td>
<td>7.5</td>
<td>7.5</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>25.5</td>
<td>25.5</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>36</td>
<td>36</td>
</tr>
</tbody>
</table>

3.3 Nanoclay deposition on the GRE composite laminate

3.3.1 Materials

3.3.1.1 Nanoclay

An alkyl quaternary ammonium modified montmorillonite, Cloisite 30B (Southern Clay Products) was used. The clay was dried at 120 °C for 2 h and then 7 wt% was dispersed in 90 ml ethanol with 2 wt% sodium dodecyl sulphate surfactant (BDH, UK) and stirred for 24 h at room temperature.

3.3.1.2 Monomer

Hexamethyldisiloxane (HMDSO) of synthetic grade with 98% purity and specific gravity of 0.76 (Sigma-Aldrich, UK) was used
3.3.1.3 Phenolic resin binder [6]

A phenolic resin, DUREZ 33156 (Sumitomo Bakelite Europe) is a modified liquid phenolic resin containing phenol (polymer with formaldehyde) (58-78 wt%), ethanol (20-29 wt%) and water (3 wt%).

3.3.2 Deposition of nanoclays on the GRE composite laminate surface

The nanoclay coatings were prepared by using two different approaches: 1) a cold plasma technique and 2) using a binder system.

3.3.2.1 Plasma equipment and process

The atmosphere plasma apparatus used in this experiment is described in detail elsewhere [7,8]. It consists of a Surfatron microwave cavity into which a plasma containment quartz tube was placed. This was connected to a microwave generator (SAIREM) operating at 2.45 GHz frequency with a continuous power output ranging from 0 to 300 Watts. Argon gas (99.99% purity) with a flow rate of 20 l/min was used to initiate and generate the plasma at atmosphere pressure. An argon glow discharge was generated in a fused quartz reactor chamber and the argon plasma ignited by striking using a copper wire. A constant distance of 10 mm was maintained between the tip of quartz tube containing plasma flame and the sample surface. For the plasma treatment with the hexamethyldisiloxane (HMDSO) monomer, the argon gas was bubbled through the HMDSO monomer, which is a liquid at room temperature under atmospheric pressure. Argon (Ar) serves as a carrier gas and an Ar-HMDSO plasma was created.
3.3.2.2 Nanoclay coating using Ar-plasma (30B/Ar coating)

Before any surface treatment, the GRE laminates (size 75 x 75 mm) were cleaned with acetone. Three step processes were employed to prepare this coating. In the first step, the composite laminates were treated with an atmospheric argon plasma, Ar-plasma, (flow rate 20 l/min; P= 150W; t = 15 s per 100 mm) for activating and roughening the surface at the nano/macro level. In the second step, a homogenous nanoclay suspension in ethanol was sprayed on the activated substrate using an air-brush (model BD-138; tip = 0.5 mm; air pressure = 15 PSI) and layer-by-layer (LbL) technique adapted from the procedure used by other researchers [9,10]. During the building-up of the coating layer through spraying, the first two layers are the most important for uniformity of application of the coating and its thickness. Good adhesion of the first two layers has a major influence on the stability of further coating layers. During spraying, a 100 mm distance between the spray tip and the activated substrate is maintained. The coated sample was dried at 80 °C in an oven for 5 min after the first spraying, followed by 2 min for subsequent layers. The process was repeated until 20 layers of coating were built-up on each sample. In the final step, the coated sample was dried again at 80 °C in the oven for 30 min to evaporate any residual solvent and then treated with argon plasma (flow rate 20 l/min; P= 150W; t = 15 s per 100 mm) to activate the cross-linking between nanoclay and the epoxy polymer on the surface. This coating procedure is shown in Figure 3.3.

Figure 3.3: Procedure for the nanoclay deposition using the Ar-plasma

3.3.2.3 Nanoclay coating using Ar/HMDSO-plasma (30B/HMDSO coating)

The procedure adapted for this coating was similar to that used for nanoclay coating using Ar-plasma (Section 3.3.2.2), except for the use of the Ar/HMDSO plasma instead
of the Ar-plasma for the surface activation in the first step. The Ar/HMDSO plasma was obtained by bubbling the argon gas through the HMDSO liquid prior to creating a plasma. After depositing 20 layers by the LbL technique and drying the coating in an oven at 80 °C for 30 min, the coated sample was exposed to an Ar-plasma, similar to that used for the 30B/Ar coating in Section 3.3.2.2. The procedure is shown in Figure 3.4.

![Figure 3.4: Procedure for the nanoclay deposition using the Ar/HMDSO-plasma and the Ar-plasma](image)

### 3.3.2.4 Nanoclay coating using a phenolic resin as binder (30B/Phe coating)

For this coating a phenolic resin (DUREZ 33156) was used as a binder. The coating formulation was prepared by adding 10 wt% of phenolic resin into 20 ml of the nanoclay dispersion solution described in the above sections.

![Figure 3.5: Procedure for the nanoclay deposition using the phenolic resin binder](image)

The mixture was stirred at room temperature using a magnetic bar (magnetic stirrer hotplate from: Bibby HC502) at a high speed (1300 rpm) for 3 h. The surface of GRE laminate (75 x 75 mm size) was cleaned with acetone to remove any impurities and then
dried at room temperature for 10 min before spraying the nanoclay and the binder mixture on the surface of the laminate using an air-brush. The coating was applied layer-by-layer (LbL) to build up 20 layers of coating for each sample, using parameters similar to those used for other two nanoclay coatings. The coated samples were then cured at room temperature for 24 h and then post-cured at 80 °C for another 12 h. This coating procedure is illustrated in Figure 3.5.

In order to quantify the concentration of clay on the GRE composite surfaces, all nanoclay coated laminates were weighed before and after coating application and the wt% clay deposited on the surface was calculated as in following equation (1):

\[
\text{Clay deposition (wt%) = } \frac{W_{\text{clay}} - W_0}{W_0} \times 100
\]  

Where \( W_0 \) is weight of the virgin laminate and \( W_{\text{clay}} \) is weight of the coated laminate.

In case of 30B/HMDSO coating, \( W_{\text{clay}} = \) total weight of coating - weight of HMDSO. Weight of HMDSO was measured by weighing GRE laminate before and after Ar/HMDSO plasma activation.

In case of 30B/Phe coating, \( W_{\text{clay}} = 0.9 \times \) total weight of coating (10 wt% of the coating is phenolic resin)

### 3.4 Ceramic nano/micro particulate coatings

#### 3.4.1 Materials

##### 3.4.1.1 Ceramic particles

(i) Fumed nanosilica (Si): Aerosol 200 (Evonik Industries), a high purity amorphous anhydrous colloidal silicon dioxide with a specific surface area of 200 m²/g.

(ii) Nanoclay (30B): Cloisite 30B (Southern Clay Products), a commercially available alkyl quaternary ammonium modified montmorillonite clay.

(iii) Low melting glass (Ce): Ceepree (M.&C.T Ltd., UK), a blend of glass frits (low-melting silicate glass), in a white powder form of 30-50 µm particle size.
(iv) Glass flake (Flek): Flekashield (NGF Europe, UK), platelets of E-glass of ~ 5 µm thickness and 10-4000 µm width.

(v) Aluminium titanate (Re): Recoxit (Ohcera.Co., Ltd., Japan), a resist-corrosion-oxide powder, composed of aluminium titanate ($\text{Al}_2\text{TiO}_5$).

(vi) Zirconia (Zr): XZO1357 (Mel Chemical, UK), an aqueous dispersion of yttria doped zirconia, which consists of 91-93 wt% zirconia and 7-9 wt% yttrium oxide.

3.4.1.2 Resin binder

(i) Epoxy resin: Araldite LY5052 and Aradur CH 5052 system as discussed in Section 3.1.1.1.

(ii) Flame retarded epoxy: Firetex DP1600 (Leighs’ Paints, UK) formulation. The details have already been discussed in Section 3.2.1.1. This resin is a DOPO (9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide) modified epoxy resin. This is a commercial product. Hence, the exact composition is not known. It is guessed that DOPO content is about 10 wt%.

(iii) Flame retardants (FRs) used in epoxy resin binder. Additive FRs:

- Ammonium polyphosphate, Amgurd MC(APP, Rhodia, UK)
- Pentaerythritol phosphate, NH1197 (Chemtura, UK)
- Tris (tribromoneopentyl) phosphate, FR372 (ICL, Israel)

(iv) Phenolic resin: DUREZ 33156 (Sumitomo Bakelite N.V.) [6]

3.4.2 Application of ceramic particulate coatings on the GRE composite laminate

Three sets of samples were prepared. In Set I, flame retarded epoxy (DP1600) binder was used in the ceramic particle coatings. In Set II, three commercial flame retardants were used in the epoxy resin to evaluate the fire retardant efficiency of each of the flame retarded epoxy resin binder when applied on the laminate surface. Phenolic resin was also used in this set. In Set III, the ceramic particle coatings were prepared using phenolic resin as the binder.
3.4.2.1 Set I: Ceramic particle coatings using a flame retarded epoxy resin as binder

Three commercially available ceramic powders (Ceepree, Reoxit and zirconia, Section 3.2.3) were used to prepare the ceramic particle coatings of approximately 1 mm thickness on 75 mm X 35 mm GRE composite samples. The coatings were prepared using the DP1600 epoxy resin system containing 10 wt% DOPO. Firstly, the ceramic powders (70 wt%) and a DP1600 base resin (30 wt%) were dispersed in methyl ethyl ketone (MEK, 50 wt% w.r.t. mixture of epoxy resin and ceramic powder). The suspension was stirred with a mechanical stirrer for 10 min. The DP 1600 hardener (30 wt% w.r.t. DP1600 base resin) was added to the mixture and it was stirred for another 5 min. Each GRE laminate (75 X 35 mm) was individually coated by the coating mixtures of Ceepree, Reoxit and zirconia. This coating procedure is presented in Figure 3.6. Samples are named as GRE-DP/Ce, GRE-DP/Zr and GRE-DP/Re, respectively.

![Figure 3.6: Procedure for applying ceramic particle coatings using the epoxy binder](image)

These three coatings were applied by a roller and paint brush to obtain coatings of approximately 1 mm thicknesses. The coated samples were then cured at room temperature for 12 h and post-cured at 80 °C for 6 h. To quantify the concentration of ceramic particles on the GRE composite surface, all coated laminates were weighed before and after coating application and the wt% ceramic particles deposited on the surface was calculated as in following equation (2):

\[
\text{Ceramic particle deposition (wt\%) } = \frac{W_{\text{Ceramic}} - W_o}{W_o} \times 100
\]

Where \( W_o \) is weight of the virgin laminate; \( W_{\text{Ceramic}} = f_c \times W_{\text{coating}} \) (\( W_{\text{coating}} \) is total weight of the coating and \( f_c \) is the fractional mass of ceramic part, e.g. 0.7 in case of 70 wt% particles in the coating)
3.4.2.2 Set II: Coating containing only resin binder with and without additional flame retardants

In order to study the flammability behaviour of the different resins to be used as a coating binder, GRE laminates (75 mm x 75 mm) were individually coated on the surface with the four different flame retarded epoxy resins and a phenolic resin using following procedure.

**GRE-EP/FR:** 20 wt% of an FR (APP, NH1197 or FR372) was added into the epoxy resin (Araldite LY5052). The mixture was stirred by a mechanical stirrer until the flame retardant was uniformly dispersed at room temperature and then 30 wt% hardener (Aradur CH5052) was added into the mixture. Approximately 0.5 g of flame retarded epoxy was used and uniformly applied on the clean surface of a GRE composite laminate by a roller and paint brush technique, similar to that used for the coatings in Section 3.4.2.1 to obtain 100-130 µm coating thicknesses. The coated samples were then cured at room temperature for 12 h and post cured at 80 °C for 6 h.

**GRE-Phe:** 0.5 g of phenolic resin (DUREZ33156) was applied on the clean surface of GRE composite using a small paint brush. The phenolic coated GRE laminate was cured at room temperature for 12 h and post cured at 80 °C for 24 h.

3.4.2.3 Set III: Ceramic particle coatings using a phenolic resin as binder

Based on the flammability behaviour of samples in described Section 3.4.2.2, the phenolic resin has been selected and used as a binder for the final set of ceramic particle coatings. Five types of ceramic particles: nanoclay, nanosilica, Flekashield, Recoxit and zirconia (see Section 3.4.1), were used to prepare coatings of approximately 100-600 µm thicknesses. The ceramic particle and phenolic resin ratio for each coating was different depending upon the type of each ceramic particle as presented in Table 3.2. The ceramic : resin ratio of each ceramic coating type was established based upon the maximum amount of particle component that can be added into the phenolic binder. It was not possible to increase the level of ceramic particle in the coatings further than those given in Table 3.2 without adversely affecting processability of the coating, which becomes too viscous and cannot allow uniform application on the GRE composite laminate.
Table 3.2: The ceramic particle : phenolic resin ratio of different coatings on laminate specimens

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ceramic type in the coating</th>
<th>Ceramic : Phenolic resin mass ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>GRE-P/30B</td>
<td>Nanoclay</td>
<td>25:75</td>
</tr>
<tr>
<td>GRE-P/Si</td>
<td>Nanosilica</td>
<td>10:90</td>
</tr>
<tr>
<td>GRE-P/Flek</td>
<td>Flekashield</td>
<td>20:80</td>
</tr>
<tr>
<td>GRE-P/Re</td>
<td>Recoxit</td>
<td>70:30</td>
</tr>
<tr>
<td>GRE-P/Zr</td>
<td>Zirconia</td>
<td>70:30</td>
</tr>
<tr>
<td>GRE-P/FZr</td>
<td>Flekashield and Zirconia</td>
<td>10Flek:20Zr:70</td>
</tr>
</tbody>
</table>

Two sets of coated GRE composite laminates were then prepared using two different approaches; a) ceramic particle with resin binder and b) ceramic particle coatings with an additional particle layer on the surface.

a) Ceramic coatings on GRE composite using a phenolic binder

These ceramic particle coatings were prepared by dispersing the ceramic powders in a phenolic resin binder using the proportion given in Table 3.2. The procedure adapted for these coatings was similar to that used for ceramic particle coatings using the flame retarded epoxy binder (Section 3.3.4.1), except that 10 wt% ethanol was used as a solvent instead of the methyl ethyl ketone (50 wt% w.r.t. mixture of binder and ceramic powder). Furthermore, in order to increase the uniform distribution of the particles in the surface coating, a K-bar coater (200 µm spirally wound bar, R.K Print-Coat Instruments Ltd) was used to apply the coating formulation on the GRE composite laminates (size 75 mm x 150 mm). Following the uniform coating, the coated laminates were then cured at room temperature for 12 h and then post-cured at 80 °C for 24 h. Similarly, a sample with only a phenolic resin coated on the GRE laminate was also prepared in order to compare the effect of the binder on these ceramic particle coatings.

b) Ceramic particle coatings with extra ceramic particle deposition

For this set extra ceramic particles were deposited on samples prepared as discussed above in (a). Only Flekashield, Recoxit, zirconia and a combination of Flekashield/ Zirconia (1:2 ratio) particles were used in this set of samples. The first step of coating preparation was similar to the one discussed above (Section 3.3.4.3 (a)), but while the resin in the coating was still uncured, dry ceramic particles were deposited on the surface.
by sieving using either a 50 mesh (300 µm) or a 100 mesh (150 µm) depending on the size of each ceramic particle to achieve 300-600 µm thick coatings. The coated samples were then cured as discussed in Section 3.3.4.3 (a). This coating procedure is presented in Figure 3.7. These samples prepared with additional particles sieved on the top are named as GRE-P/FlekS, GRE-P/ReS, GRE-P/ZrS and GRE-P/FZrS. The thickness of each coating was measured using a digital calliper.

Figure 3.7: Procedure for applying ceramic particle coatings with additional ceramic particles on the coated samples

For ceramic coatings on the GRE composite using the phenolic binder, the wt% ceramic particle deposited was calculated by the same method as for the coating in Section 3.3.4.1. The \( W_{\text{Ceramic}} \) is calculated from the ratio between ceramic particle and phenolic resin in Table 3.2. In the sample containing additional particles deposited on the ceramic surface coating, the wt% ceramic particles deposited on the surface was calculated using equation (3):

\[
\text{Ceramic particle deposition (wt%)} = \left[ \frac{W_{\text{Coating}} - (W_{\text{wet}} \times \text{Binder (wt%)})}{W_{o}} \right] \times 100 \tag{3}
\]

Where \( W_{o} \) is weight of the virgin laminate, \( W_{\text{Coating}} \) is total weight of the coating and \( W_{\text{wet}} \) is weight of ceramic in the coated samples before the particle deposition.

### 3.5 Chemical coating

#### 3.5.1 Materials

(i) Monomer (VPA): Vinyl phosphonic acid (Rhodia Inc. [11]), a colourless liquid containing vinylphosphonic acid (75-90 wt%), (2-hydroxyethyl) phosphonic acid (5-10
wt%), 2-chloroethylphosphonic acid (1-5 wt%), 1,2-ethane diposphonic acid 91-5 (1-5 wt%), vinyl phosphonic acid dimer (1-5 wt%) and orthophosphonic acid (1-5 wt%)

(ii) Crosslinking agent: triallyl isocyanurate, TAICROS® (TCI Europe N.V.)

(iii) Photo-initiator: 2-hydroxy-2-methylpropiophenone, Darocur1173 (TCI Europe N.V.)

![Chemical structures](image)

**Figure 3.8:** Chemical structures of (a) VPA monomer, (b) triallyl isocyanurate and (c) Darocur1173

### 3.5.2 Polymerisation of monomers on the GRE composite laminate

The monomer, vinyl phosphonic acid (VPA), crosslinker triallyl isocyanurate (5 wt% w.r.t. VPA) and photo-initiator Darocur 1173 (5 wt% w.r.t. VPA) were used to polymerise the VPA coating on the GRE composite substrate. All the chemicals were mixed and stirred by hand until a homogenous dispersion was achieved. The mixture was then applied on the GRE composite surface (75 mm x 150 mm) using a paint brush to obtain coatings of 300 and 500 µm thicknesses. The mass of the coating mixtures required to achieve 300 and 500 µm thick coatings are given in Table 3.3.

**Table 3.3:** Details of different coating thicknesses of VPA coated on the GRE laminate specimens (size 150 mm x 75 mm)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Coating thickness (µm)</th>
<th>Coating mass (g)</th>
<th>VPA coating formulations (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Monomer</td>
</tr>
<tr>
<td>GRE-0.3VPA</td>
<td>300</td>
<td>7 ±1</td>
<td>7</td>
</tr>
<tr>
<td>GRE-0.5VPA</td>
<td>500</td>
<td>12 ±1</td>
<td>12</td>
</tr>
</tbody>
</table>
An in-house UV chamber was constructed to house the photo-polymerisation process. The chamber consisted of a ventilated MDF box containing six 15 watt black light bulbs having a peak emission at 360 nm wavelength. It was observed after the initial experiments that film polymerisation was vastly improved if air was excluded from the sample. A separate smaller sample chamber was constructed using a thin plate aluminium box with part of the lid removed and a thin foil of overhead transparency film was attached to seal the lid, which still allows UV transmission. The wet coated sample was placed in this container and the container was then purged with nitrogen gas (99.99% purity with flow rate of 10 l/min) in order to eliminate the scavenging effect of oxygen during photo-polymerisation. The distance between the UV light source and this container was also maintained as 3 cm. This UV polymerisation procedure is illustrated in Figure 3.9. After UV irradiation for 5 h (300 µm thick) and 6 h (500 µm thick), the VPA-coated GRE laminate was removed from the UV irradiator and then post-cured at 80 °C for 24 h in an oven. At the end, the thickness of each coating was measured using a digital calliper.

3.6 Physical, morphological and surface characterisations

Each coated sample was weighed before and after application of the coatings, in order to calculate the % coating deposition, as discussed in previous sections. The thickness of each coating was obtained from the difference of the thicknesses of coated and uncoated samples, measured using a digital calliper. Several techniques were also used to characterise the physical/chemical properties of the uncoated and coated glass fibre-reinforced epoxy composite (GRE) samples.
3.6.1 Scanning electron microscopy (SEM)

The morphologies of GRE surfaces coated with different coatings were studied using scanning electron microscopy (SEM, Hitachi Technologies Model 3400). Before observation, the GRE samples with/without surface coatings were cut into 5 mm x 5 mm sizes and coated with gold in a mini sputter coater (Quorum Technologies Ltd., UK Model: SC7620). Then, the surface of the sample was scanned with an accelerating voltage capacity 1-20 k eV, the working distance was 20 mm and magnification ranged between 10X to 350,000X at 15 kV providing resolution from 1 mm down to 100 µm.

The particle sizes of the Flekashield, Recoxit and zirconia were also determined from SEM images by measuring each individual ceramic particle using a image analysis software (Image J, National Institute of Health/USA) [12]. Measurements were performed on 20 particles chosen from each of five different regions of the micrographs to ensure adequate statistical confidence.

3.6.2 Infrared attenuated total reflection spectroscopy (IR-ATR)

The identification of chemical functional groups of plasma-treated, nanoclay and VPA coated surfaces of GRE laminate were studied by infrared attenuated total reflection spectroscopy (IR-ATR, Nicolet iS10, Thermo Scientific). The principle of the technique involves detecting the IR transmittance bands of the surface coatings on the GRE laminate and comparing with the spectrum of the control sample. In this technique, the sampling depth can be up to ~ 1 µm or more. IR also allows investigation of the polymerisation of the VPA monomer.

3.6.3 Surface wettability

A water drop test was carried out to evaluate the wettability of the GRE laminate surfaces. This test is the best method for estimating the change in a substrate nature occurring due to plasma application and a surface coating [13]. In this experiment, a dropper containing a methylene blue solution (dissolved 1.0 g of methylene blue in 1 litre distilled water) was held at 50 mm distance above the sample surface as shown in Figure 3.10. A digital video camera was used to record from the time when the drop falls on the sample surface until 120 s later. The shape and nature of water droplet on the surface of
each sample was observed and used to identify the surface properties, i.e. wettability, hydrophilicity and hydrophobicity in a similar way to that reported in the reference [14].

Figure 3.10: Water drop test set up

3.7 Flammability and thermal barrier properties evaluation

3.7.1 Flammability testing by cone calorimeter

The flammability and fire properties of all the GRE composite laminates with/without surface coatings was evaluated by a cone calorimeter (Fire Testing Technology (FTT)), according to ISO 5560 [15]. A cone calorimeter can provide material “reaction to fire” information for use in evaluating the fire hazard of materials. According to this standard, the size of a typical cone calorimeter specimen (100 mm x 100 mm) is mounted on a horizontal specimen holder, which is placed on the load cell under the cone heater of set irradiance (0-100 kW/m²). The distance between each specimen and the cone heater can be altered by adjusting the pedestal height to ensure there is a 25 mm gap between the top of the specimen and the cone heater (Figure 3.11).

Figure 3.11: Image of the FTT cone calorimeter
The load cell records the weight of the sample during the experiment. When the sample is heated, volatiles are ignited with an electric spark igniter located 13 mm above the centre of the specimen. The volatiles extracted through the exhaust duct with set orifice flow rate (24 l/s) are fed into an oxygen analyser, which measures the amount of oxygen consumed. The principle of the cone calorimetry is that net heat of combustion is proportional to the amount of oxygen required for combustion. Approximately 13.1 MJ of heat is released per kilogram of oxygen consumed. The rate of smoke released every second is measured from the liberated smoke opacity in the exhaust duct with respect to light transmittance from a laser (632.8 nm wavelength) to a photocell detector located cross the duct. The transmittance is recorded by the cone software. The higher the smoke opacity means lower the light transmission. The total smoke production is obtained by summing up the rate of smoke release over the burning period. Similarly, the concentration of other combustion products such as carbon monoxide (CO) and carbon dioxide (CO₂) can be measured using a CO/CO₂ analyser. From these data, the primary fire properties can be obtained by cone calorimetry. Those used in this work are briefly summarised below.

*Time to ignition (TTI, s) and flame out time (FO, s):* As the name implies, TTI is the time required for a sample to ignite when exposed to a fire or an external heat flux. FO is the period from initiation to extermination of the fire and describes how easily or how fast a burning sample will eventually be self-extinguished.

*Heat release rate (HRR, kW/m²):* HRR is the amount of thermal energy generated, per unit area of surface, when a sample is exposed to a fire or an external heat flux. The cone calorimeter also can record specific rates of heat release such as the peak heat release rate (PHRR, kW/m²) and total heat release (THR, MJ/m²).

*Mass loss:* During combustion, the change in mass of the sample per second is recorded by the load cell. The mass loss from a sample is measured by comparing the initial and the final masses of the sample at the end of each test. The remaining residue at the end of burning is known as the char residue.

The fire properties mentioned above have been used to assess the flammability and thermal barrier properties of the GRE composites and the coatings dealt with in this work. However, the smoke release and CO/CO₂ productions are not considered. In previous work in our laboratories, a comparative study of different sizes of samples has been
undertaken to study the variation of the results [16]. This study is based upon changing the area of samples from 100 cm$^2$ (a square 100 mm x 100 mm size) for the standard cone test to 56.25 cm$^2$ for a square 75 mm x 75 mm size. The results showed that these two different areas produced similar PHRR, THR and EHC values. Therefore, the 75 mm x 75 mm size of a specimen was used for all described samples in order to compare the flammability of different coatings in terms of TTI, FO, PHRR, T$\text{PHRR}$ and THR with respect to the control samples. Tests were carried out in accordance with the ISO 5660 standard, using a range of incident heat fluxes (from 20 to 50 kW/m$^2$) in the horizontal mode at a distance of 25 mm from the cone heater. Before testing, the back surface (unexposed) and the edges of the samples were wrapped with aluminium foil to ensure that only top surface would be exposed to the cone heater. The samples were ignited in the presence of an electric spark igniter. However, in some cases the samples were tested in the absence of an electric spark igniter so that any exposed resin on the surface, which does not easily ignite and thermal barrier effectiveness of the coatings can be studied. Three replicate tests were performed on the control and all the surface coated samples. The cone calorimeter test conditions for each coating type studied in this work are given in Table 3.4.

Table 3.4: Details of the cone calorimeter test conditions for each type of coating

<table>
<thead>
<tr>
<th>Coating types</th>
<th>Heat flux (kW/m$^2$)</th>
<th>Electric spark igniter</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>With</td>
</tr>
<tr>
<td>Intumescent coatings</td>
<td>50</td>
<td>✓</td>
</tr>
<tr>
<td>Nanoclay depositions</td>
<td>35</td>
<td></td>
</tr>
<tr>
<td>Ceramic particle coatings using FR epoxy resin binder</td>
<td>20, 30, 40 and 50</td>
<td>✓</td>
</tr>
<tr>
<td>Ceramic particle coatings using phenolic resin binder</td>
<td>35 and 50</td>
<td></td>
</tr>
<tr>
<td>Chemical coatings</td>
<td>35 and 50</td>
<td></td>
</tr>
</tbody>
</table>

As evident from Table 3.4, most of the coatings were tested at two heat fluxes. 35 kW/m$^2$ was chosen to evaluate their thermal barrier effectiveness in a typical small, growing fire scenario [17], while 50 kW/m$^2$ heat flux was chosen to study their efficiency to provide a thermal barrier as well as fire protection to the GRE composite laminates in a real-fire scenario [17]. Nanoclay depositions were tested only at 35 kW/m$^2$ as the coating was too thin to provide fire protection. Furthermore, except for intumescent coatings and one set
of ceramic particle coatings, spark ignition was not used. It was noted while testing ceramic particle coatings that any exposed resin on the surface ignites easily and then the true thermal barrier effectiveness of the coating cannot be accurately evaluated. To avoid this, in the rest of the testing, spark ignition was not used.

3.7.2 Char expansion study of intumescent coatings

Char expansion of intumescent coatings M90, M93 and FX5002 (see Section 3.2) and coated GRE samples were measured using different techniques.

3.7.2.1 Char expansion measurement after cone experiments

The thicknesses of the residual chars left from the GRE samples coated with different intumescent coatings at the end of each cone calorimeter test was measured in order to study the expansion of the coatings. The specimen thickness was measured before and after the tests. The char expansion was calculated using equations (4) and (5).

\[
\text{Char thickness} = T_1 - T_0
\]  
\[ (4) \]

Where \( T_0 \) is original thickness of the laminate and \( T_1 \) is final thickness of the laminate after the test.

\[
\text{Char expansion ratio} = \frac{\text{Char thickness}}{\text{Coating thickness}}
\]  
\[ (5) \]

3.7.2.2 Char expansion as a function of temperature measurement using the Advanced Rheometric Expansion System (ARES)

An Advanced Rheometric Expansion System (ARES 20A, Rheometric Scientific) with a concentric cylinder sample holder was used to evaluate the char expansion of the M90, M93 and FX5002 intumescent coatings as a function of temperature. The intumescent coating samples of circular shape with 25 mm diameter and of 1 mm thickness were used. All tests were performed under a dynamic temperature ramp from 25 °C to 500 °C in strain-controlled mode over 1.5-3.0 gmf force range with 5 and 10 °C/min heating rates, 1.0 rad/sec frequency range and 1% strain limits. Three replicate specimens of each coating were tested and the results were averaged.
3.7.2.3 Char expansion as a function of time measurement using an infrared camera in a mass loss calorimeter

The expansion of M90, M93 and FX5002 intumescent coatings as a function of time during exposure to an incident heat radiant heat of 50 kW/m$^2$ in the presence of an electric spark ignite in a mass loss cone calorimeter was observed by a FLIR (ThermaCAM™ A40) infrared camera. This experiment set up is shown in Figure 3.12.

![FLIR system, Thermo vision A40](image)

**Figure 3.12:** The experimental set up for char expansion as a function of time study by using a cone calorimeter and Thermo-Vision A40 infrared camera

The distance between sample’s surface and cone heater was kept as 35 mm in all tests. The infrared camera was programmed to record temperatures between 50°C to 1500 °C and images were recorded at 5 s intervals for test periods of 300 s for GRE composite samples and 1000 s for intumescent coatings. Two specimens of each sample were tested for reproducibility. The char expansion data were evaluated by using image analysis software (ThermoCAM Researcher program) from the movie obtained from the infrared camera.

3.7.3 Temperature measurements for thermal barrier properties

In order to study the thermal barrier property and thermal insulating effect of each type of coating, the temperature measurements were taken during the cone calorimeter experiments (see Section 3.4.2) as the heat is transferred from the cone heater through the thickness of the samples. For temperature measurements, three K-type thermocouples were placed, one on top of the surface coating, one underneath the coating and the other
on the back surface (unexposed) of each sample. The thermocouples were connected to a Recorders data logger and the temperature profiles were recorded as a function of exposure time.

The thermocouple ends were carefully positioned as to be in alignment with the centre of the radiant heater in order to increase heat conduction efficiency. This set up is demonstrated in Figure 3.13 (a). Similarly, the temperatures of other coatings were also measured, but the three $K$-type thermocouples were placed, one on top of the coating surface and other two on the back surface of each sample as shown in Figure 3.13 (b).

**Figure 3.13: Schematic representation for thermal barrier measurement of (a) intumescent coatings and (b) nanoclay depositions, ceramic particle coatings and chemical coatings**

The thermocouple ends were carefully positioned as to be in alignment with the centre of the radiant heater in order to increase heat conduction efficiency. This set up is demonstrated in Figure 3.13 (a). Similarly, the temperatures of other coatings were also measured, but the three $K$-type thermocouples were placed, one on top of the coating surface and other two on the back surface of each sample as shown in Figure 3.13 (b).

### 3.7.4 Thermal conductivity measurements using the hot disk method

Thermal conductivities of three intumescent coatings were measured by the hot disk method at either room temperature or high temperature. The hot disk method is a well known method for measuring temperature dependent thermal conductivity of materials from 0.005 to 500 W/mK and covering a temperature range from 30 to 1000 K. In this method, the hot disk sensor was placed in between two sample pieces in the Transient Plane Source (TPS). The sensor recording of the mean temperature of the sample combined with a parameter estimation from the thermal constant analyser makes it
possible to estimate thermal conductivity and thermal diffusivity of the samples from a single experiment [18,19].

3.7.4.1 The thermal conductivity measurement at room temperature

Before the experiment was performed, the intumescent coating samples were prepared in 50 mm diameter round shapes with 5 mm thickness, similar to that used in Sections 3.3.1 and 3.4.2.3. The thermal conductivity values of these coatings were measured at room temperature by a hot disk thermal constant analyser (Hot Disk TPS 2500 S, Thermo-concept, Bordeaux, France).

![Figure 3.14: a) The experimental setup for thermal conductivity measurement at room temperature, b) the sample in the sample holder and c) the guarding cylinder](image)

Figure 3.14 illustrates a typical experimental setup as the hot disk sensor is placed between two sample pieces and installed in the guarding cylinder. The sensor is directly connected to the thermal constant analyser in order to measure the thermal conductivity of the sample at room temperature. Power was applied at 0.01- 0.08 W for 10 to 40 s, depending on the thermal conductivity of each sample. All tests were run in duplicate and the results averaged.
3.7.4.2 The thermal conductivity measurement at high temperatures

The thermal conductivity values of M90, M93 and FX5002 intumescent coatings at different temperatures ranging from 20 to 700 °C were measured by a hot disk thermal constant analyser (Hot Disk TPS 2500 S), Figure 3.15.

![Image of thermal conductivity measurement setup](image)

**Figure 3.15**: a) The arrangement for thermal conductivity measurement at elevated temperatures b) the sample in the sample holder and c) the sample holder in the furnace

The M90, M93 and FX5002 samples were prepared from chemicals in round moulds of 25 mm diameter and 1 mm thickness, and then the hot disk sensor and two pieces of each coating sample were bonded by using a small amount of intumescent mixture on the sample as a glue to ensure a good contact between the sample and the sensor during the experiment. The experimental set up for the thermal conductivity measurement at elevated temperatures is shown in Figure 3.15. The furnace and the sample holder are specially designed to permit the expansion and the degradation of the sample as a function of temperature [20]. The furnace is purged with flowing nitrogen to prevent the oxidation of the sensor. A cooling system was also connected to the furnace for measuring the thermal conductivity of the material at a particular temperature. The conductivity measurements were made by applying a power of 0.05–0.19 W for 10 - 80 s, depending on the thermal conductivity of each sample at a particular temperature. One sample of each type was tested. The sample was heated to a particular temperature and held at that temperature for...
3-5 min before the reading was taken. The temperature was raised to the next required value and thermal conductivity readings again taken. These experiments were conducted at room temperature, 200, 300, 400, 500, 600 and 700 °C. The reported thermal conductivity values at all temperatures are an average of three measurements taken at that particular temperature.

3.8 Mechanical testing

This section focuses on the mechanical behaviour of the GRE composite and laminates coated with (1) ceramic particle coatings using phenolic resin binder and (2) chemical coatings.

3.8.1 Impact drop weight test

The effect of all ceramic particle coatings on the impact properties of GRE composite was investigated using an impact drop weight test at two different impact energy conditions. The specimen size for this impact drop weight test was fixed as 75 mm x 75 mm, the thickness varied from sample to sample. A Dynatup Mini-Tower drop weight impact with a 16 mm diameter hemispherical tup was used to perform the test at 1 J impact energy loading. The test set up is illustrated in Figure 3.16.

![Impact drop weight test setup](image)

**Figure 3.16: Impact drop weight set up for assessing impact performance**

The test specimen was placed on the centre of the sample holder, which had a hole of 76.2 mm diameter, and clamped via a hydro-operated clamp. Following this, the installed
specimen was impacted by a steel impactor of 16 mm crosshead diameter and a mass of 1.03 kg, dropped from 100 mm height to produce an impact velocity of 1.38 m/s. For 5 J impact energy loading, a Instron-Dynatup 9250 HV drop weight impact of similar diameter hemispherical tup as the one discussed above was employed. In this case, the steel impactor was of mass 4.62 kg and dropped from 110 mm height to produce an impact velocity of 1.46 m/s. During the test, the high-speed data acquisition system has the capability of storing the entire impact event and hence measured acceleration/deceleration as a function of time. From this raw data, using numerical integration, the load-time, load-deflection, and energy-time curves were produced. The digital images of the samples after the impact tests were studied to investigate the damage to the coatings. In this study, the damage of the coatings after the weight drop impact test at 1 and 5 J impact energies can be classified as (1) visible surface damage due to impact tup in a local area, (2) debonding of coating and (3) cracking of coating. These are demonstrated in Table 3.5.

**Table 3.5: The coating fracture types from impact drop weight tests**

<table>
<thead>
<tr>
<th>Visible surface damage</th>
<th>Debonding</th>
<th>Cracking</th>
</tr>
</thead>
</table>

Two replicate specimens of each sample were tested at each impact energy loading and then the impact modulus \( E_i \) of each sample was calculated using equation (6).

\[
E_i = \frac{3 \times D}{4\pi h^3} \text{ (K)}
\]  

(6)

Where \( D \) = Diameter of hole of the sample holder; \( h \) = thickness; \( K \) = initial stiffness determined from the load vs. deflection curve

### 3.8.2 Three point bending test

The three point bending test was carried out to determine the flexural modulus of the GRE composites with/without surface coatings at room temperature using a Universal Instron 3369 machine. A specimen size of 125 mm x 13 mm was used for this test. The
thickness varied depending on the type of coating. The tests on all samples were performed in a displacement-controlled mode with a 100 N load cell applied at 1 mm/min until the flexural deflection reaches 2 mm. The length span between the supports was 100 mm and the load was applied at the midpoint of the coating surface of the specimen, as shown in Figure 3.17.

![Figure 3.17: Three point bending test setup for assessing flexural performance](image)

This test condition (load strain) was such that the composites could fully recover their original flexural properties. To confirm that the test specimens completely recovered, three loading–unloading cycles were performed on each specimen. During the test, the high-speed data acquisition system stored the entire flexural bending event and then produces load vs. displacement curves. The flexural modulus ($E_f$) of the samples was calculated based upon the Engineers’ bending theory [21] as presented in following equation.

$$E_f = \frac{L^3}{4bh^3} (K)$$

(7)

Where $L$ = the test span; $h$ = thickness; $b$ = width; $K$ = initial stiffness determined from the load vs. displacement curve

### 3.8.3 Three point bending flexural test on heat/fire damaged samples

The effect of radiant heat on the flexural properties of GRE composites specimens was investigated by exposing the coated surface of the composite laminate specimens (125 mm x 13 mm) to different radiant heat fluxes and different times under the cone heater,
maintaining 25 mm distance between radiant heat source and the specimen. In this test, two replicate specimens of each sample were exposed to heat as:

- Exposed to 25 kW/m$^2$ for 60, 120 and 240 s
- Exposed to 50 kW/m$^2$ for 30 s

These conditions were selected based on the cone results from Section 3.7.1. The selected radiant heat fluxes and times were to ensure that the sample should not ignite. If the sample ignited, the flame was immediately quenched by a fireproof fabric followed by cooling in a ventilated room. During the exposure, the sample was insulated on all sides and the reverse (unexposed) surface, using a ceramic blanket as shown in Figure 3.18.

![Image of edge protection and sample exposure to the cone heater at different heat fluxes and different times](image)

**Figure 3.18: Edge protection and sample exposure to the cone heater at different heat fluxes and different times**

After the heat exposure, the samples were cooled down to room temperature, and then the flexural test was performed in the three-point bending mode with conditions similar to that used for non-heat damaged samples in Section 3.8.2. The flexural load was applied on the heat damaged surface so that the damaged surface would bear the compressive strain. The flexural modulus after heat exposure was calculated using the original thickness of the sample. In the most damaged samples, the thickness did not change after heat exposure. The observed flexural moduli were then compared to the room temperature value of the same specimen. The modulus retention of each heat damaged sample was calculated using equation (8), where $E_{fu}$ is the flexural modulus of undamaged sample and $E_{fd}$ is the flexural modulus of the damaged sample.

$$\text{Flexural modulus retention (\%) = } \frac{E_{fu}}{E_{fd}} \times 100$$  \hspace{1cm} (8)
3.9 Durability of coatings

The durability of nanoclay, ceramic particle and chemical coatings to water and peeling were tested in order to study the durability of these coatings.

3.9.1 Water soak test

To evaluate the effect of water and moisture under atmospheric conditions on coatings, the coated samples were studied by the water-soak test, according to BS EN ISO 2812-2:2007 standard [22]. This method enables the determination of the effects of water on an individual layer or a multi-layer system of coating materials and the assessment of the damage to the substrate. In this test, 35 mm x 35 mm sized specimens of GRE laminates with/without surface coatings were used. Two replicates of each sample were tested. As mentioned in the BS EN ISO 2812-2:2007 standard, the four edges of all samples were sealed with an epoxy resin (AralditeLY5052 and Aradur 5052 hardener), which is the same as used for the resin matrix of the GRE composite. The resin was applied on the edges with a paint brush. After sealing the edges, the samples were then cured at room temperature for 12 h and post-cured at 80 °C for 6 h. All samples were first dried at 100 °C in an oven for 2 h, weighed and then fully immersed in 100 ml of deionised water. For each sample, a separate container was used and the water containers were covered with aluminium foil. After keeping the samples for 24 h at room temperature, the samples were removed, dried at room temperature for 24 h and then at 100 °C for 2 h. All samples were then weighed again. The images of the sample were also taken using a digital camera before and after the test to investigate the morphologies of the coating surfaces. The weight loss of each sample (wt%) was calculated via equations (9) and (10).

For control sample:  \[ \% \text{ Weight loss} = \frac{W_B - W_A}{W_B} \times 100 \]  (9)

In cases of coated sample:  \[ \% \text{ Weight loss} = \frac{W_B - W_A}{W_C} \times 100 \]  (10)

Where \( W_A \) = weight after finished the process of the test, \( W_B \) = initial weight before test and \( W_C \) = weight of the coating.
3.9.2 Tape pull test

The tape pull test was performed to evaluate the adhesion between a coating and the laminates, similar to the ones specified in BS EN ISO 2409:2007 [23] and ASTM D3359 [24], which are often used to examine the adhesion of films or sheets to an adhesive [25]. The adhesion could be evaluated by the bonding strength at the interface between coating and substrate. When adhesive failure is obtained, the separation between coating and substrate could be observed.

![Figure 3.19: Tape pull test with pulling at 180° angle](image)

Initially, a piece of Sellotape was applied on the surface of the coated laminate and smoothed with fingers to ensure good contact. Holding the sample with one hand, the tape was then peeled back at 180° angle in one smooth movement with the other hand as displayed in Figure 3.19. The test was done at three different locations on the same sample (size 75 mm x 75 mm) for each coated sample. The images of the sample were also taken using digital camera before and after the test. To evaluate the failure of the coating, the % weight loss was calculated using a similar equation to the one in Section 3.9.1, and the % coating peeled (wt%) was evaluated using equation (11).

\[
\% \text{ Peeling of the coating} = \left[ \frac{W_2 - W_1}{W_1} \times 100 \right] \times 100 \tag{11}
\]

Where, \(W_1\) and \(W_2\) are the weights of the coated samples before and after the tape pull test. The % Coating deposition from different coating types is discussed in Sections 3.3.2.4, 3.4.2.2 and 3.4.2.3.
3.10 References

[1] Araldite LY 5052 and Aradur 5052 CH, Huntsman, Safety Data sheet


Chapter 4

INTUMESCENT COATINGS

In this chapter the thermal barrier effect of three commercial intumescent coatings on glass fibre-reinforced epoxy (GRE) composites has been studied with a view of setting a benchmark to evaluate the performance of other coatings being developed in subsequent chapters. Three different commercial coatings from Leigs’ Paints (UK), M90, M93 and FX5002 of 1, 3 and 5 mm thicknesses were applied on the surfaces of the GRE composite as discussed in Section 3.2 (Chapter 3). Both M90 and M93 coatings contain an epoxy resin binder, the M93, in addition, contains ~10 wt% DOPO (9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide). FX5002 is a water based coating. The flammability and thermal barrier properties of the uncoated and coated GRE composites were studied by a cone calorimeter at 50kW/m² heat flux in the presence of an ignition source and related to the char expansion efficiency of these coatings. Thermal conductivities of the chars as a function of time have also been studied. These parameters have been used in predicting the surface requirements of an ideal coating that can enable a given composite structure to survive a defined thermal threat for a specified period of time.

4.1 Physical properties of the coatings

The coating thickness and mass of each intumescent coating on the surfaces of GRE laminates are given in Table 4.1.
Table 4.1: Physical properties of the coatings, referring to the amount applied on a 75 mm x 75 mm plaque of GRE laminates

<table>
<thead>
<tr>
<th>Intumescent coating</th>
<th>Sample</th>
<th>Laminate thickness (mm)</th>
<th>Mass of coating (g)</th>
<th>Coating thickness (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>M90:epoxy based</td>
<td>GRE-M90-1</td>
<td>2.38 ±0.06</td>
<td>6.40 ±0.17</td>
<td>1.52 ±0.40</td>
</tr>
<tr>
<td></td>
<td>GRE-M90-3</td>
<td>2.42 ±0.11</td>
<td>15.41 ±0.05</td>
<td>3.35 ±0.41</td>
</tr>
<tr>
<td></td>
<td>GRE-M90-5</td>
<td>2.40 ±0.05</td>
<td>27.21 ±0.19</td>
<td>5.71 ±0.49</td>
</tr>
<tr>
<td>M93:epoxy based; contains DOPO</td>
<td>GRE-M93-1</td>
<td>2.37 ±0.05</td>
<td>6.60 ±0.04</td>
<td>1.66 ±0.35</td>
</tr>
<tr>
<td></td>
<td>GRE-M93-3</td>
<td>2.40 ±0.01</td>
<td>15.47 ±0.07</td>
<td>3.14 ±0.23</td>
</tr>
<tr>
<td></td>
<td>GRE-M93-5</td>
<td>2.45 ±0.08</td>
<td>27.19 ±0.07</td>
<td>5.83 ±0.22</td>
</tr>
<tr>
<td>FX5002:water based</td>
<td>GRE-FX5002-1</td>
<td>2.37 ±0.12</td>
<td>6.66 ±0.78</td>
<td>0.83 ±0.18</td>
</tr>
<tr>
<td></td>
<td>GRE-FX5002-3</td>
<td>2.39 ±0.12</td>
<td>24.05 ±1.43</td>
<td>3.00 ±0.11</td>
</tr>
<tr>
<td></td>
<td>GRE-FX5002-5</td>
<td>2.38 ±0.10</td>
<td>36.17 ±3.78</td>
<td>4.78 ±0.82</td>
</tr>
</tbody>
</table>

4.2 Flammability behaviour of GRE composites with intumescent coatings

The data collected from the cone calorimetric tests at 50 kW/m² with an ignition source (Section 3.7.1, Chapter 3) were analysed in terms of time-to-ignition (TTI), flame out time (FO), peak heat release (PHRR), time-to-PHRR (T_{PHRR}) and fire growth index (FIGRA), and are given in Table 4.2. The heat release rates as a function of time curves of all GRE laminates with varied thicknesses of intumescent coatings are graphically plotted in Figure 4.1 (a - d). The thickness of all coated samples was also measured after cone exposure and char thicknesses and char expansion ratios were calculated. These results are also presented in Table 4.3. In this section, the flammability behaviour of GRE composites coated with different intumescent coatings are discussed, firstly, for the 1 mm coating thickness in order to observe the effect of different coatings on the overall fire performance of the composites and secondly, for different thicknesses in order to observe the effect of coating thickness on the improvement in flame retardant performance. It is to be noted that all intumescent coatings used in this work are commercial samples, and their exact composition is not known, and hence, here only their flammability properties are discussed without relating to the effect of individual components of the chemical formulations.
Figure 4.1: HRR versus time curves of the control and coated samples of (a) 1 mm coating of each type; 1, 3 and 5 mm coatings of (b) M90, (c) M93 and (d) FX5002 at 50kW/m² with an ignition source.
Table 4.2: Cone calorimetric data for different intumescent coatings of varying thicknesses on GRE composite samples exposed to 50 kW/m² heat flux with an ignition source

<table>
<thead>
<tr>
<th>Sample</th>
<th>Coating thickness (mm)</th>
<th>TTI (s)</th>
<th>FO (s)</th>
<th>1st Peak PHRR (kW/m²)</th>
<th>TPHRR (s)</th>
<th>2nd Peak PHRR (kW/m²)</th>
<th>TPHRR (s)</th>
<th>THR (MJ/m²)</th>
<th>FIGRA* (kW/m²-s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>-</td>
<td>49 ±2</td>
<td>180 ±26</td>
<td>733 ±35</td>
<td>91 ±3</td>
<td>-</td>
<td>-</td>
<td>38.8 ±0.6</td>
<td>8.1 ±0.7</td>
</tr>
<tr>
<td>GRE-M90-1</td>
<td>1.27 ±0.01</td>
<td>44 ±1</td>
<td>340 ±11</td>
<td>131 ±9</td>
<td>74 ±1</td>
<td>321 ±25</td>
<td>205 ±21</td>
<td>50.8 ±0.7</td>
<td>1.6 ±0.01</td>
</tr>
<tr>
<td>GRE-M90-3</td>
<td>2.96 ±0.16</td>
<td>46 ±1</td>
<td>790 ±7</td>
<td>96 ±1</td>
<td>75 ±1</td>
<td>115 ±14</td>
<td>405 ±30</td>
<td>51.5 ±0.4</td>
<td>0.3 ±0.01</td>
</tr>
<tr>
<td>GRE-M90-5</td>
<td>5.28 ±0.22</td>
<td>44 ±1</td>
<td>1340 ±75</td>
<td>128 ±6</td>
<td>77 ±1</td>
<td>108 ±2</td>
<td>617 ±21</td>
<td>109.4±5.4</td>
<td>0.3 ±0.01</td>
</tr>
<tr>
<td>GRE-M93-1</td>
<td>1.35 ±0.02</td>
<td>35 ±3</td>
<td>430 ±11</td>
<td>113 ±33</td>
<td>57 ±2</td>
<td>176 ±33</td>
<td>262 ±14</td>
<td>42.9 ±9.5</td>
<td>0.7 ±0.10</td>
</tr>
<tr>
<td>GRE-M93-3</td>
<td>2.95 ±0.09</td>
<td>38 ±3</td>
<td>838 ±33</td>
<td>123 ±3</td>
<td>59 ±3</td>
<td>150 ±7</td>
<td>473 ±3</td>
<td>72.1 ±3.1</td>
<td>0.4 ±0.10</td>
</tr>
<tr>
<td>GRE-M93-5</td>
<td>5.72 ±0.09</td>
<td>37 ±4</td>
<td>1560 ±119</td>
<td>96 ±11</td>
<td>59 ±3</td>
<td>94 ±14</td>
<td>814 ±92</td>
<td>76.1 ±11.5</td>
<td>0.1 ±0.01</td>
</tr>
<tr>
<td>GRE-FX5002-1</td>
<td>0.94 ±0.03</td>
<td>20 ±2</td>
<td>210 ±12</td>
<td>126 ±6</td>
<td>47 ±1</td>
<td>55 ±3</td>
<td>134 ±10</td>
<td>26.6 ±0.1</td>
<td>0.4 ±0.01</td>
</tr>
<tr>
<td>GRE-FX5002-3</td>
<td>2.91 ±0.09</td>
<td>17 ±1</td>
<td>242 ±32</td>
<td>106 ±1</td>
<td>47 ±1</td>
<td>54 ±1</td>
<td>385 ±15</td>
<td>31.2 ±0.7</td>
<td>0.1 ±0.01</td>
</tr>
<tr>
<td>GRE-FX5002-5</td>
<td>5.25 ±0.82</td>
<td>19 ±2</td>
<td>268 ±26</td>
<td>127 ±4</td>
<td>48 ±4</td>
<td>53 ±1</td>
<td>541 ±27</td>
<td>32.8 ±0.4</td>
<td>0.1 ±0.10</td>
</tr>
</tbody>
</table>

Note: FIGRA index = PHRR divided by TPHRR (kW/m²-s) of 2nd Peak
<table>
<thead>
<tr>
<th>Sample</th>
<th>Char residual images</th>
<th>Exposure time (s)</th>
<th>Char thickness (mm)</th>
<th>Expansion ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td></td>
<td>200</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>GRE-M90-1</td>
<td></td>
<td>500</td>
<td>6.8 ± 2.2</td>
<td>5.3 ± 1.8</td>
</tr>
<tr>
<td>GRE-M90-3</td>
<td></td>
<td>900</td>
<td>10.0 ± 2.0</td>
<td>3.4 ± 0.4</td>
</tr>
<tr>
<td>GRE-M90-5</td>
<td></td>
<td>1400</td>
<td>15.8 ± 0.9</td>
<td>3.0 ± 0.4</td>
</tr>
<tr>
<td>GRE-M93-1</td>
<td></td>
<td>500</td>
<td>9.8 ± 2.8</td>
<td>7.2 ± 2.2</td>
</tr>
<tr>
<td>GRE-M93-3</td>
<td></td>
<td>900</td>
<td>20.7 ± 1.3</td>
<td>7.0 ± 0.1</td>
</tr>
<tr>
<td>GRE-M93-5</td>
<td></td>
<td>1600</td>
<td>27.2 ± 2.7</td>
<td>4.8 ± 0.4</td>
</tr>
<tr>
<td>GRE-FX5002-1</td>
<td></td>
<td>800</td>
<td>24.1 ± 2.6</td>
<td>25.6 ± 1.5</td>
</tr>
<tr>
<td>GRE-FX5002-3</td>
<td></td>
<td>800</td>
<td>41.7 ± 2.4</td>
<td>14.3 ± 0.8</td>
</tr>
<tr>
<td>GRE-FX5002-5</td>
<td></td>
<td>1200</td>
<td>36.3 ± 4.5</td>
<td>6.9 ± 0.7</td>
</tr>
</tbody>
</table>
Figure 4.1 (a), the heat release (HRR) curve shows that in the uncoated GRE composite laminate (control) there is a single sharp, but narrow peak, terminating within 200 s, indicating a short duration of burning. When the laminate is exposed to the cone heater, the temperature of exposed surface rapidly increases, resulting in decomposition of the resin matrix while gaseous volatiles are released. When the volatiles reached a critical mass flux, in the presence of the spark ignition source, these combustible volatiles ignite. Immediately following ignition, the surface temperature of the laminate rapidly increases due to the burning of the laminate. The control sample ignited at 49 s following by a rapid increase in the heat release rate reaching a peak (PHRR) value of 733 kW/m$^2$ at 91 s and a rapid reduction in the HRR which mirrors the conclusion of the flaming combustion process (Table 4.2).

Figure 4.1 (a) also shows that the HRR-curve for GRE-M90-1 is very different from the control sample, being less intense, but broader with two peaks, indicating a longer burning duration. Generally, the intumescent coatings upon heating produce expandable char. An intumescent formulation contains three components, an acid source (e.g. ammonium polyphosphate), a char former (e.g. pentaerythritol) and a blowing agent (e.g. melamine). On heating, the acid source produces an acid, which catalyses the dehydration reactions of the char former, resulting in the formation of char. In the meantime, the blowing agent produces inert gas, which inflates the char [1,2]. The thickness, coherence and porosity of the char determine its thermal barrier efficiency. The first peak in Figure 4.1 (a) is due to ignition and burning of the binder resin of the coating formulation. In the meantime, the intumescent reactions are activated and char is formed, which suppresses the burning of underlying laminate, resulting in a slow increase in HRR. The insulating effect of the intumescent char layer is clear from the drop in HRR after the initial ignition. However, after prolonged exposure to heat, the intumescent char oxidizes and degrades and the underlying resin starts burning, representing the second PHRR. The interval between the first and the second HRR peaks indicates the thermal durability of the intumescent char. From Figure 4.1 (b), GRE-M90-3 and GRE-M90-5 with coating thicknesses 3 and 5, respectively show similar HRR behaviour as GRE-M90-1. However, the peak is less intense, but broader, resulting in a significant decrease in the peak value. With increase in coating thickness and its char thickness, the interval between two peaks
of HRR increases and the intensity of the second PHRR decreases, indicating the stability and thermal barrier efficiency of the intumescent char. The PHRR values for the second peak of GRE-M90-1, GRE-M90-3 and GRE-M90-5 samples are 321, 115 and 108 kW/m² respectively (see Table 4.2), which correspond to a 50-85% reduction relative to the control sample. However, as can be noted from Table 4.2, all M-90 coated samples ignite slightly earlier than the control sample and the coating thickness has no significant effect on TTI, and intensity and time to the first PHRR. This is due to the fact that the binder resin of the intumescent coating ignites at similar time regardless of the coating thickness. However, the 3 and 5 mm thick coatings provided a thicker char layer which is a better insulator resulting in reduction in heat release rate during continued radiant heat exposure. These observations can be related to the char expansion results obtained at the end of the test as shown in Table 4.3. The char thickness from GRE-M90-1 has the least thickness (6.8 mm) followed by GRE-M90-3 (10 mm) and GRE-M90-5 (15.8 mm). Similarly, the time to reach the second (main) peak HRR (T_{PHRR}) was also significantly prolonged by a thicker intumescent char. This also helped in reducing the FIGRA values. The FIGRA (Fire growth index) can identify a materials’ potential fire safety [3]. The FIGRA values for GRE-M90-3 and GRE-M90-5 are very low (~0.3 kW/m²-s) compared to control sample (8.1 kW/m²-s), which reflects the thermal barrier efficiency of the M90 char coating. The coating thickness has no effect on TTI, but flame out time increased from 1 to 5 mm thickness, resulting in higher THR values compared to the control laminate, which further increased with increasing thickness. The PHRR value for the second peak, however, significantly decreased from 1 to 3 mm coating and was not further affected by increasing coating thickness to 5 mm. These results suggest that M90 epoxy-based intumescent coating provided a thermally insulating expanded char on GRE composite surface to prevent heat transfer and a rapidly growing fire. The optimal coating thickness providing a char thick enough to provide efficient thermal protection lies between 1 and 3 mm.

M93 coating is also an epoxy-based intumescent coating, similar to M90 and the epoxy resin contains ~ 10 wt% of DOPO and ~ 1 wt% triphenyl phosphate (see Section 3.2.1, Chapter 3). As can be seen in Table 4.2, TTI values of GRE-M93 samples are reduced compared to GRE-M90 samples. DOPO-containing epoxy resin has been reported in the
literature to decompose at a lower temperature and igniting earlier than the control resin [4]. This suggests that M90 and M93 epoxy-based intumescent coatings used in this work cannot delay time-to-ignition. As can be seen from Figure 4.1 (a and c), the pattern of the HRR curves of GRE-M93 samples is similar to those observed for GRE-M90, but the second peak is less intense and time interval between the first and second peak HRR is longer than in the GRE-M90. This is reflected by the lower PHRR values of 176, 150 and 94 kW/m² for the GRE-M93-1, GRE-M93-3 and GRE-M93-5 samples, respectively. THR values are also lower than the M90 coated samples while the T_{PHRR} values for the second (main) peak are delayed, resulting in further reduction in FIGRA value. The FIGRA in GRE-M93-5 is reduced to 0.1 kW/m²·s. This indicates that M93 coating provides further improvement in fire resistance and also has higher thermal barrier efficiency than the M90 coating at respective coating thicknesses. This can be explained by the char expansion results (Table 4.3), showing that GRE-M93-1 sample has the highest char expansion ratio (7.2), followed by GRE-M93-3 (7.0) and GRE-M93-5 (4.8) has the least char expansion ratio. For all coated samples the char expansion ratio decreases with increasing coating thickness. The higher expansion of M93 compared to M90 indicates that the presence of DOPO and other phosphorus compounds in the M93 coating contribute to a higher char expansion and the expanded char provides more fire resistance than the char of the M90 coating. The effect of coating thickness is similar to that of M90, i.e. no effect on TTI, flame out time increase, PHRR decreases and THR increases. The optimal thickness is 3 mm.

The application of the water-based intumescent coating (FX5002) provides the shortest TTI values, which is due to the flammable nature of vinyl acetate/vinyl ester copolymer binder used in this coating as opposed to less flammable epoxy resin binder in the other two coatings. However, the expansion of the coating starts earlier than other coatings. On comparing with GRE-M90-1 and GRE-M93-1 samples, GRE-FX5002-1 shows a similar pattern of HRR curves in Figure 4.1 (a), but the second peak is of much lower intensity, which can be related to their higher char expansion ratio values, for instance, 25.6 for the GRE-FX5002-1 sample, which is higher than GRE-M93-1 and GRE-M93-1 by approximately 3-5 times (see Table 4.3). The 24 mm thick char from GRE-FX5002-1 provided very low PHRR (55 kW/m²) for the second peak. Further increase in char
thicknesses from 3 and 5mm coatings (samples GRE-FX5002-3 and GRE-FX5002-5), there was no further reduction in PHRR. The FIGRA values for GRE-FX5002-3 and GRE-FX5002-5 are also very low (~ 0.1 kW/m²·s) compared to that of the control sample. The superior flame retardant efficacy of FX5002 coating can be demonstrated by the significant reduction in THR values compared with the control sample.

The effect of the thickness of all the coatings is better observed from Figure 4.2 where Δ parameters of TTI, PHRR, THR and FIGRA are plotted as a function of coating thickness. The expression Δ parameter is taken as difference in the particular parameter (TTI, PHRR etc.) of the coated sample and the control sample. The results in Figure 4.2 show that the coating thickness of each coating has a minimal effect on TTI (Figure 4.2 (a)). However, PHRR slightly decreased from 1 to 3 mm coating and was not further

\[ \Delta \text{TTI} \]
affected by increasing coating thickness to 5 mm. This behaviour can be explained by the fact that when expanded char becomes very thick, it gets closer to the cone heater and hence, the incident heat flux gets higher than that for the sample kept at the 25 mm distance in the cone experiment. A similar trend is observed for the FIGRA values (Figure 4.2 (b and c)). The THR values increased at respective coating thicknesses, except for FX5002, which significantly decreased from 1 to 5 mm coating as clearly seen in Figure 4.2 (d). The effectiveness of these three coatings, considering ± 10% experimental error, can be ranked as:

In terms of TTI reduction: \( M90-3 > M93-3 > FX5002-1 \)

In terms of PHRR reduction: \( FX5002-5 < M93-5 \approx M90-5 \)

In terms of THR reduction: \( FX5002-1 < M90-1 \approx M93-1 \)

In terms of FIGRA reduction: \( M93-5 \approx FX5002-3 < M90-3 \)

These observations suggest that the optimum thickness of the coating lies between 1 to 3 mm, which can provide thermal barrier efficiency in order to reduce PHRR by > 50%, increase \( T_{PHRR} \) up to 100 s and decrease FIGRA values by > 80% of that of the GRE composite.

At the end of the cone calorimeter tests, in the control sample, all the resin was burnt, and only layers of glass fabric were left as shown in Table 4.3. With the presence of the intumescent coatings, the structural integrity of GRE composites coated with 1, 3 and 5 mm thick coatings of M90, M93 and FX2005 can be seen from the digital images of residual char in Table 4.3. These results show that all three coatings provide passive fire protection to composite laminates, resulting in a considerable delay in time to total loss of structural integrity of the laminate (delamination) after exposure to 50 kW/m². The control sample delaminated after 200 s heat exposure time. However, all the coated samples delaminated after ~400 s for 1 mm, ~800 s for 3 mm and ~1200 s for 5 mm thick coatings as seen from the images in Table 4.3.
4.3 Thermal barrier effect of the intumescent coatings

Thermal barrier effect of these intumescent coatings was investigated by measuring the temperature at the surface ($T_S$) and the back surface (un-exposed) of the laminate ($T_B$) during cone calorimetric tests at 50 kW/m$^2$ heat flux (Section 3.7.3, Chapter 3).

![Temperature graphs](image)

**Figure 4.3**: The surface ($T_S$) and back surface ($T_B$) temperatures as a function of time for the control and M90, M93 and FX5002 coated samples at 50kW/m$^2$ heat flux
Table 4.4: The maximum surface (underneath coating), $T_{\text{MaxS}}$ and back surface temperature ($T_{\text{MaxB}}$) and time to reach those temperatures of all the GRE composite samples exposed to 50 kW/m$^2$ heat flux

<table>
<thead>
<tr>
<th>Sample</th>
<th>Surface temperature</th>
<th>Back surface temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$T_{\text{MaxS}}$ ($^\circ$C)</td>
<td>$t_{\text{MaxS}}$ (s)</td>
</tr>
<tr>
<td>Control</td>
<td>720</td>
<td>156 ± 13</td>
</tr>
<tr>
<td>GRE-M90-1</td>
<td>757</td>
<td>372 ± 34</td>
</tr>
<tr>
<td>GRE-M90-3</td>
<td>501</td>
<td>600 ± 25</td>
</tr>
<tr>
<td>GRE-M90-5</td>
<td>540</td>
<td>900 ± 58</td>
</tr>
<tr>
<td>GRE-M93-1</td>
<td>752</td>
<td>434 ± 24</td>
</tr>
<tr>
<td>GRE-M93-3</td>
<td>577</td>
<td>731 ± 47</td>
</tr>
<tr>
<td>GRE-M93-5</td>
<td>533</td>
<td>900 ± 49</td>
</tr>
<tr>
<td>GRE-FX5002-1</td>
<td>654</td>
<td>368 ± 17</td>
</tr>
<tr>
<td>GRE-FX5002-3</td>
<td>314</td>
<td>806± 1</td>
</tr>
<tr>
<td>GRE-FX5002-5</td>
<td>277</td>
<td>843 ± 2</td>
</tr>
</tbody>
</table>

Note: $T_{\text{MaxS}}$ = maximum temperature at surface; $T_{\text{MaxB}}$ = maximum temperature at back surface; $t_{\text{MaxS}}$ = time to reach $T_{\text{MaxS}}$, $t_{\text{MaxB}}$ = time to $T_{\text{MaxB}}$; $\Delta t$ indicates an increase w.r.t the control value.

To evaluate the effect of each type of intumescent coating on the thermal barrier effectiveness, temperature values obtained from both temperatures ($T_S$ and $T_B$) are plotted in Figures 4.3. The maximum values of temperatures obtained and time to reach those temperatures for all GRE composites samples are reported in Table 4.4. It is to be noted that in the control sample, the thermocouple was placed on the surface, and hence, is an estimated surface temperature, whereas, for the coated laminates, the temperature measured was underneath the coating and represents the temperature on the surface of the laminate, underneath the coating.

Figure 4.3 (a) shows the variation of the surface temperature underneath the coating layer ($T_S$) as a function of exposure time for GRE-M90-1, GRE-M90-3 and GRE-M90-5 compared to the surface temperature of control sample (without coating). These temperature profiles can be used to indicate the thermal barrier efficiency of these coatings only without considering the inherent thermal barrier effect of the glass fibre.
reinforcement matrix in the GRE composite substrate. The uncoated GRE composite (control) shows a rapid rise in the surface temperature reaching the highest value of 720°C only after 156 s (Table 4.4), resulting in a high slope (Figure 4.3 (a-c)), which indicates very high rate of temperature rise at the surface of uncoated GRE composite. Figure 4.3 (a) also shows that the application of M90 coatings of varied thickness resulted in a reduction of the rate of temperature rise of the GRE composite surface temperature, shown by a lower slope of the temperature-time curve. GRE-M90-5 shows the slowest rise in the surface temperature underneath coating layer (T_{Max} 540 °C after 900 s) compared with GRE-M90-3 (501 °C after 600 s) and GRE-M90-1 (757 °C after 372 s) (Table 4.4). GRE-M90-1 provides the least protection from heat penetration. The observed results are consistent with the char expansion as shown in Table 4.3. The residual char thickness can be ordered as GRE-M90-5 > GRE-M90-3 > GRE-M90-1.

In Figure 4.3 (b), M93 coated samples show similar temperature profile patterns as the M90 coated samples, both being epoxy-based intumescent coatings. However, the surface temperature rise of M93 coated samples is slightly lower than those of the M90 coating, indicated by longer time to reach T_{MaxS} for coatings of similar thickness. The effectiveness can be ranked as GRE-M93-5 (533 °C, 900 s) > GRE-M93-3 (577 °C, 731) > GRE-M93-1 (752 °C, 434 s). Samples, GRE-FX5002-1, GRE-FX5002-3 and GRE-FX5002-5 (Figures 4.3 (c)) show different surface temperature-time curve patterns from those of the GRE-M90 and GRE-M93 samples. The surface temperature constantly rose in the first 200 s after which the temperature rise is slower and keeps almost constant until the end of test. This is probably due to the expanded char formation up to 200 s, which is thicker than any other chars (see Table 4.3). The intumescent char on the exposed surface effectively slows down heat penetration, which reduces the temperature increase rate. Moreover, the FX5002 coated samples show a slower rise in the surface temperature underneath coating and a lower T_{MaxS} than the other two coated composites. GRE-FX5002-5 shows the longest time to reach the maximum temperature of the surface of the laminate, 277 °C after 843 s, followed by GRE-FX5002-3 (314 °C, 806 s) and GRE-FX5002-1(654 °C, 368 s).
For a surface coating to be an effective thermal barrier, it should stop the surface of the laminate reaching the softening temperature of the resin. In a laminate, when the temperature reaches the softening or the glass transition temperature ($T_g$) of the epoxy resin, the mechanical properties of the laminate are lost [5]. As an effective thermal barrier protection, the coating should stop or retard the temperature rise at the surface reaching the softening temperature (the glass transition temperature ($T_g$)) or the pyrolysis temperature (the temperature at which maximum mass loss occurs) of the epoxy resin. The $T_g$ of epoxy resins commonly is a 150-220 °C, and for the resin used in this work, it is 180 °C. The curves in Figure 4.3 (a-c) show that within 120 s, the surface temperatures of all coated samples have already reached the softening temperature of the resin (180 °C), except, for GRE-M90-5 and GRE-M93-5 which required a much longer time, i.e. >300 s. These results can be more clearly seen in Figure 4.4 (a-b), which shows the time required for the surface and back surface of the composites to reach the softening temperature of 180 °C and the pyrolysis temperature of 250 °C. The results show that the surface temperature of the control sample reaches the softening temperature within 28 s, when the samples is protected by 1 mm thick coating, there is no significant delay in time (32-38 s) to reach 180 °C. However, a 3 mm thick coating significantly delayed the time to reach 180 °C by 65-110 s. For 5mm coatings, the time was increased to over 300 s for M90 and M93 coatings, whilst for the FX5002 the time was 353 s, which is not much different than that for the 3mm thick coating. A similar effect is seen for the time required to reach the pyrolysis temperature of the resin (250 °C) on the surface for all coated samples. The 1mm coating is not very effective. Among the 3 mm thick coatings, GRE-FX5002-3 shows the longest time (223 s) and all 5 mm thick coatings are effective and take > 470 s to reach 250 °C compared to 37 s in the control sample. That means with the 1 mm coatings of GRE-M90, GRE-M93 and GRE-FX5002, the GRE composite will start losing its mechanical properties in a short period of time after exposure to a high heat source. Coatings of $\geq$ 3 mm thickness could provide longer times to retain the mechanical properties.
Figure 4.4: The time required for the composite to reach (a) 180 °C and (b) 250 °C at the surface and back surface for the control, M90, M93 and FX5002 coatings at 1, 3 and 5 mm thicknesses when exposed to 50 kW/m² heat flux.

Figure 4.3 (d) shows the variation of the back surface temperature (T_B) with exposure time for the M90 coated samples with thicknesses from 1, 3 and 5 mm and the control sample. The rapid increase of temperature at back surface of the control sample can be observed. The control sample reaches the maximum temperature of 592 °C within 202 s (Table 4.4). The rapid increase in temperature is due to the fact that in the control sample, the heat on the exposed surface is conducted through the bulk of the composite without inhibition. As expected, the M90, M93 and FX5002 coatings provide thermal protection for the GRE composite, resulting in slower temperature rises at the back surface (slope
decreased) compared to the control sample as shown in Figure 4.3 (d-f). The slower rise in temperature can be clearly seen by the increase in time to reach the maximum back surface temperature ($T_{\text{MaxB}}$). GRE-M90-1, GRE-M90-3 and GRE-M90-5 reduced the maximum temperature to 528, 501 and 423 °C, while increasing the time to reach the maximum temperature, i.e. 372, 600 and 900 s, respectively. These results are consistent with the surface temperature profiles of M90 coated samples in Figure 4.3 (a). The penetration of heat into the underlying GRP composites is dependent on the thickness of the coating. The increasing coating thickness provided a positive effect on the retardation of heat penetration. In relation to protective char performance, the thickest expanded residual char from 5 mm coating thickness provides a higher thermal barrier efficiency than observed for 3 mm and 1 mm coatings, respectively. An increase in time to reach similar maximum temperature at back surface was observed in samples containing M93 coatings, GRE-M93-1, GRE-M93-3 and GRE-M93-5 increased in time as 434, 718 and 900 s to reach 520, 481 and 423 °C, respectively. With the FX5002 coatings, the coated samples showed the lowest maximum temperature and a much increased time to reach the maximum temperature at the back surface compared to the other coatings. GRE-FX5002-1, GRE-FX5002-3 and GRE-FX5002-5 reduced the maximum back surface temperature to 501, 291 and 255 °C, while increasing the time to reach the maximum temperature of 600, 871 and 843 s, respectively.

For clear comparison of the thermal barrier efficiency of each coating, the difference between the temperature at surface (below the coating layer) and the back surface of all GRE composites as function of time was determined and results for same thickness, but different coatings, are plotted in Figure 4.5. Higher temperature difference indicates the higher thermal barrier effect by the insulative char to delay/retard the temperature rising within the GRE composite laminate structure. In the first 90 s, all M90, M93 and FX5002 coated laminates showed similar differences in temperature between surface and back surface as the control laminate, indicating that the thermal protective char layer of these three intumescent coatings took approximately 90 s to be formed. After 90 s, the M90, M93 and FX5002 coatings provided a higher thermal insulative char performance to prevent heat penetration through the composite laminate.
Figure 4.5: The difference in surface and back surface temperatures of the GRE composites as a function of time with the M90, M93 and FX5002 coatings of (a) 1, (b) 3 and (c) 5 mm thicknesses exposed to 50kW/m² heat flux.

For 1 mm thick coatings, the thermal barrier effectiveness of the different coatings can be ranked as GRE-FX5002-1 ≈ GRE-M93-1 ≈ GRE-M90-1 (Figure 4.5 (a)). The observed order of efficiency with respect to thermal protection of the 3 mm coating thickness laminates is GRE-FX5002-3 ≈ GRE-M93-3 > GRE-M90-3 (Figure 4.5 (b)). With the 5 mm coated laminates (Figure 4.5 (c)), FX5002, M93 and M90 coatings provided similar thermal barrier efficacy. In terms of the time to reach a surface temperature of 180 °C, the thermal barrier efficiency of the coatings can be ranked as GRE-M93-5 ≈ GRE-M90-5 > GRE-FX5002-5 and to reach 250 °C; GRE-M95-5 ≈ GRE-FX5002-5 > GRE-M90-5. Hence, coating FX5002 is more effective than the others. These observations are consistent with the reduction in magnitude of the HRR results in Section 4.2.
4.4 Quantification of thermal barrier efficiency of coatings

As mentioned earlier, a crucial feature of any fibre-reinforced polymeric structural composite is the thermal and burning behaviour of its matrix resin, which affects the mechanical performance of the composite at elevated temperatures and may ultimately lead to complete loss of structural integrity. The results in the previous section have shown that intumescent surface coatings can inhibit, or reduce, the heat transfer from the fire/heat source to the underlying structure, thus helping in retaining mechanical properties of the composites on exposure to heat/fire. To evaluate the thermal barrier effectiveness of a coating on a fibre-reinforced polymeric composite laminate, it is important to predict the thermal barrier behaviour of the coating at elevated temperatures. This is also important because without predictive tools based on a thorough understanding of the subject, reliance on experiments alone are expensive and will, at best, only give information specific to the test conditions. Having an accurate knowledge about the material properties is essential if a correct and meaningful process modeling is to be performed. Thermal properties such as thermal conductivity are important parameters to simulate the temperature variation inside the polymer during a specific process. Thermal conductivity describes a material’s ability to transport heat. Thermal gradients of polymers / composites throughout the thickness of the samples are invariably used for heat transfer modeling [6,7,8,9].

In this part, the temperature dependent thermal conductivities of different coatings and their relationship with time/temperature dependent char expansion has been studied. This work was performed at Ecole Nationale Supérieure de Chimie de Lille (ENSCL), University Lille 1, France, through the Short Term Scientific Mission (SMST), sponsored by EU COST MP1105 FLARETEX project.

The main purpose of this work is four folds:

1. To quantify of the char expansion under different heating conditions
2. To measure of thermal conductivities of intumescent coatings at room and elevated temperatures
3. To observe the relationship between thermal conductivity and char thickness
4. To obtain various parameters (such as thermal conductivities at elevated temperatures and relative char thicknesses at those temperatures; temperature of the char etc.) to be used for development of a numerical model for prediction of the surface thermal requirements that an ideal coating should possess in the first instance that would enable a given composite structure to survive a defined thermal threat for a specified period of time.

4.4.1 Char expansion as a function of time by using a mass loss calorimeter and an infrared camera

The char expansion of M90 (1 mm), M93 (1 mm) and FX5002 (0.5 mm) intumescent coatings as a function of time was measured in the cone calorimeter condition at 50 kW/m² using a mass loss calorimeter at the University of Lille. The expansion was observed by an infrared camera (FLIR, ThermoCAM™ A40). This study is important as it reflects the char expansion in a real fire situation, where the heating rate is ~200 °C/min (estimated from the slope of the temperature profiles in Figure 4.3).

Figure 4.6: The char expansion vs. time curves and images of residual chars of M90 M93 and FX5002 intumescent coatings exposed to 50 kW/m² heat flux for 900 s
Figure 4.7: The intumescent char formation of M90-1mm, M93-1mm and FX5002-0.5mm during cone calorimetric tests at 50 kW/m$^2$ heat flux for 900 s
In this experiment, a constant heat flux is applied under which the char expands very quickly and once the surface temperature stabilizes, the char expansion/oxidation behaviour becomes time dependent. The char expansion was recorded digitally with an infrared camera and the data were analysed using an image analysis software (Thermo CAM researcher program) from the movie obtained from the infrared camera. From the movie, snap shots were taken at particular times and are presented in Figure 4.6. The extracted data from the video images recorded as a function of time are also plotted as shown in Figure 4.7.

As can be seen from Figure 4.6, both M90 and M93 coatings started expanding immediately and the rate of expansion was very high until 80 s, after which expansion was slower and became constant after ~ 300 s. For the FX5002 coating, the char kept expanding until 450 s and then stopped. The images of the chars obtained at the end of the experiments in Figure 4.6 also show the porous structure of the intumescent chars. The expansion process can also be clearly seen in Figure 4.7 with a sequence of infrared images taken during the formation of an intumescent char under a mass loss calorimeter. Based on these results, the FX5002 coating showed the highest char expansion and the most porous char compared to other two coatings. The char expansion of these three intumescent coatings can be ranked from high to low as:

\[ \text{FX5002 > M93 > M90} \]

### 4.4.2 Char expansion as a function of temperature

An advanced rheometric expansion system (ARES 20A, Rheometric Scientific) with a concentric cylinder sample holder was used to evaluate the char expansion as a function of temperature of the M90, M93 and FX5002 coatings. The intumescent coating samples of circular shape with 25 mm diameter and of 1 mm thicknesses were used. All tests were performed under a dynamic temperature ramp from 25 °C to 500 °C with two different heating rates (5 and 10 °C/min). For details, see Section 3.7.2.2 in Chapter 3. The char expansions as a function of temperature at different heating rates are plotted in Figure 4.8, and analysed results are given in Table 4.5.
Figure 4.8: The char thickness vs. temperature curves from rheometry of the (a) M90, (b) M93 and (c) FX5002 coatings at 5 and 10 °C/min heating rate up to 500 °C

Table 4.5: The char thicknesses at the end of rheometry experiments of the M90, M93 and FX5002 intumescent coatings at different heating rates

<table>
<thead>
<tr>
<th>Heating rate (°C/min)</th>
<th>Coating</th>
<th>Initial Thickness</th>
<th>Final char thickness</th>
<th>Char expansion ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>M90</td>
<td>2.156 ± 0.017</td>
<td>5.631 ± 0.250</td>
<td>2.6 ± 0.1</td>
</tr>
<tr>
<td></td>
<td>M93</td>
<td>2.008 ± 0.095</td>
<td>6.117 ± 0.077</td>
<td>3.1 ± 0.2</td>
</tr>
<tr>
<td></td>
<td>FX5002</td>
<td>1.394 ± 0.214</td>
<td>30.135 ± 0.545</td>
<td>22.1 ± 3.0</td>
</tr>
<tr>
<td>10</td>
<td>M90</td>
<td>1.811 ± 0.125</td>
<td>7.147 ± 0.234</td>
<td>4.0 ± 0.2</td>
</tr>
<tr>
<td></td>
<td>M93</td>
<td>1.865 ± 0.235</td>
<td>9.444 ± 0.228</td>
<td>5.1 ± 0.6</td>
</tr>
<tr>
<td></td>
<td>FX5002</td>
<td>1.107 ± 0.013</td>
<td>22.929 ± 0.441</td>
<td>20.7 ± 0.6</td>
</tr>
</tbody>
</table>

Note: Char expansion ratio = Char thickness at the end of experiment / Initial Thickness

The results in Figure 4.8 show that the three intumescent coatings on the slower heating rate expand in two distinct stages. In the first stage the char expansion is slow, whereas in the second stage expansion rate is much higher. For epoxy based M90 and M93 coatings,
the first significant expansion started at ~180 °C and then the second expansion occurred at ~300 °C. On the other hand, water based FX5002 water coating started expanding ~300 °C, followed by the second major expansion occurring after 350 °C. The effect of heating rate on char expansion of these intumescent coatings can be observed from Figure 4.8. The increase of heating rate from 5 °C/min to 10 °C/min increased the char expansion ratio of M90 from 2.6 to 4 and M93 from 3.1 to 5.1, whereas in that of FX5002, it was reduced from 22.1 to 20.7 (see Table 4.5). This is probably due to the M90 and M93 being epoxy-based intumescent coating systems, which require a higher heat treatment to build up the char, whereas the water-based intumescent coating (FX5002) could char better at the lower heating condition. Therefore, the char expansion of these three intumescent coatings under the slow heating rate can be ordered from high to low as FX5002 > M93 > M90, which is consistent with the char expansion under the constant radiant heat flux (Section 4.4.1). These results confirm that the FX5002 coating can provide higher expanded char compared to M90 and M93 coatings under all conditions.

On comparing the char formation/expansion efficiency of intumescent coatings under two different heating scenarios, i.e. a constant radiant heat flux from the cone calorimeter (Table 4.3) or slow heating conditions; i.e. using a rheometer (Table 4.5), it can be seen that with the constant high heat flux, the expansion is very quick and with the maximum expansion being slightly higher than that observed from the slow heating test in the rheometer. The results are comparable. The expansion ratio of FX5002, M93 and M90 (1 mm coating) with 10 °C/min heating rate can reach up to 20.7, 5.1 and 4.0 of its original value, while, with a fixed heat flux condition at 50 kW/m², the ratio can reach up to 25.6 (FX5002), 7.2 (M93) and 5.3 (M90).

4.5 Thermal conductivity of the intumescent coatings

The thermal conductivity (k) values of the M90, M93 and FX5002 coatings with 1 mm thickness were determined at both room temperature and elevated temperatures by using the hot disk method (see Section 3.7.4 (Chapter 3)). The observed thermal conductivity
values at every 100 °C from room temperature up to 700 °C are reported in Table 4.6 and graphically plotted in Figure 4.9.

### Table 4.6: Thermal conductivity values of the chars of intumescent coatings at different temperatures and images of residual chars obtained at the end of the test

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>M90</th>
<th>M93</th>
<th>FX5002</th>
</tr>
</thead>
<tbody>
<tr>
<td>19</td>
<td>0.32 ± 0.01</td>
<td>0.28 ± 0.01</td>
<td>0.53 ± 0.01</td>
</tr>
<tr>
<td>200</td>
<td>0.20 ± 0.01</td>
<td>0.18 ± 0.01</td>
<td>0.20 ± 0.02</td>
</tr>
<tr>
<td>300</td>
<td>0.21 ± 0.01</td>
<td>0.19 ± 0.01</td>
<td>0.19 ± 0.01</td>
</tr>
<tr>
<td>400</td>
<td>0.14 ± 0.01</td>
<td>0.15 ± 0.01</td>
<td>0.09 ± 0.01</td>
</tr>
<tr>
<td>500</td>
<td>0.19 ± 0.01</td>
<td>0.21 ± 0.01</td>
<td>0.17 ± 0.01</td>
</tr>
<tr>
<td>600</td>
<td>0.25 ± 0.01</td>
<td>0.26 ± 0.01</td>
<td></td>
</tr>
<tr>
<td>700</td>
<td>0.30 ± 0.01</td>
<td>0.34 ± 0.01</td>
<td></td>
</tr>
</tbody>
</table>

At room temperature after the test

- 0.12 ± 0.01
- 0.11 ± 0.01
- 0.06 ± 0.01

Residual char after the test

<table>
<thead>
<tr>
<th>Thickness</th>
<th>Image</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 mm</td>
<td><img src="image1.png" alt="Image" /></td>
</tr>
<tr>
<td>11 mm</td>
<td><img src="image2.png" alt="Image" /></td>
</tr>
<tr>
<td>23 mm</td>
<td><img src="image3.png" alt="Image" /></td>
</tr>
</tbody>
</table>

**Figure 4.9:** The thermal conductivity as a function of temperature of the M90, M93, FX5002 intumescent coatings
In the literature, the thermal conductivity values of intumescent char materials are reported to be varying from 0.1 W/mK to 0.4 W/mK from room temperature to 600°C [10,11]. As can be seen from results in Table 4.6, the obtained thermal conductivity values for these three coatings are within the range as reported in the literature. At room temperature, the FX5003 coating of 1 mm thickness has the highest thermal conductivity value of 0.53 W/mK compared to that of M90 (0.32 W/mK) and M93 (0.28 W/mK). The thermal conductivity of these three coatings first decreased and then increased with increasing in temperature (Figure 4.9). The first significant drop in thermal conductivity values of these M90, M93 and FX5002 intumescent coatings was observed at 200 °C (0.20 for M90, 0.18 for M93 and 0.20 W/mK for FX5002). These values remained constant until 300 °C and then decreased again, the minimum being at 400 °C, after which the values increased and kept increasing until 700 °C (see Table 4.6 and Figure 4.9). This behaviour is characteristic of an intumescent material. When exposed to high temperature, the material expands and forms a porous char structure of low heat conductivity. Hence, as the char expands due to an increase in porosity the thermal conductivity decreases. Above 400°C, the char structure does not change significantly and hence thermal conductivity increases as function of temperature [10].

Since the intumescent coatings on exposure to high temperatures expand, the thermal conductivity at a particular temperature is a measure of the thermal conductivity of the char structure at a particular expansion thickness. Therefore, the thermal conductivity results can be associated with the char expansions results obtained from rheometry in Section 4.7. To corroborate these observations, the thermal conductivity results and the char expansion results obtained from rheometry at the 10 °C/min heating rate are plotted together against temperature in Figure 4.10. The overlaid graphs in Figure 4.10 show the relationship between the thermal conductivity values and char expansion at each particular temperature of each intumescent coating.
Figure 4.10: The relationship between char expansion and thermal conductivity values vs. temperature of (a) M90, (b) M93 and (c) FX5002

It can be clearly seen that the first drop in thermal conductivity values of all intumescent coatings is due to the beginning of char expansion, at around 200 °C. The char thickness remains constant up to 300 °C while the thermal conductivity increases slightly. Further heating promotes a greater expanded char, which also means structural changes in the char (high porosity) leading to the lowest heat conductivity at 400 °C in all coatings, especially the FX5002 coating (see Figure 4.10 (c)). After 400 °C, the char structure of M90 and M93 did not change much and hence the thermal conductivity increases as a function of temperature. The maximum char expansion observed by FX5002 coating is reflected by its lowest thermal conductivity at 400 °C. It must be noted that while the trends in char expansion calculated by the rheometry can be co-related with the thermal conductivity calculated by the hot disk method, no direct relationship between the two values can be drawn due to different test conditions in both experiments. The expansion
of the char is limited in the hot disk method because of the design of the holder, while in the rheometer, the char expansion is unrestricted and hence, will be higher. After the experiments, all charred samples were cooled down to room temperature and their thermal conductivities were measured again. The results in Table 4.6 show that the thermal conductivities of all intumescent chars at room temperature are much lower than that at evaluated temperature, which is as expected. From this discussion, it can be concluded that while the thermal conductivity is an intrinsic property of a material, the changes in values with temperature are due to structural changes in the material. In case of intumescent materials it is inversely proportional to the degree of char expansion and porosity of the char [10,11,12].

4.6 Development of a numerical model

As discussed above, an intumescent coating expands upon heating and forms a porous char structure of low density, which helps in reducing the heat transfer to the underlying substrate. Therefore, the most important parameters of the expanded char affecting its thermal barrier performance are its thermal conductivity, thickness and porosity. For an ideal coating, it would be beneficial if it has low thickness when applied, produces thick char on exposure to heat and the char has minimum thermal conductivity and resistance to oxidation to be able to protect a composite structure from specified heat for a specified time. Considering these issues, in this work we have made accurate measurements of char thickness as a function of time and also its thermal conductivity as a function of time. During the thermal conductivity experiments, a porosity (heat capacity $X$ density) parameter could also be obtained. These three parameters can be used in the heat transfer equation (1) to develop a simple one-dimensional numerical heat transfer model.

$$\rho c \frac{\partial T}{\partial t} = k \frac{\partial^2 T}{\partial x^2}$$ (1)
Where: $\rho = \text{density of the coating}, \ c = \text{specific heat capacity of the coating}, \ k = \text{thermal conductivity}, \ T = \text{temperature}, \ t = \text{time} \text{ and } x = \text{thickness}$. These parameters are the properties of a coating.

Each parameter can be taken from different results in different sections and used to calculate the thermal conductivity at a particular temperature. The porosity, $\rho_c = \text{specific heat capacity x density}$, is obtained from thermal conductivity experiments (Section 4.5); the temperature ($T$) on the surface and underneath coatings, can be taken from the temperature profile results in Section 4.4; $\partial T$ in the left hand terms is the temperature difference between the surface of the coating and ambient temperature ($\sim 25 ^\circ \text{C}$); $\partial T$ on the right hand side of the equation is the temperature difference between the surface of the coating and underneath the coatings; $x$, the char thickness at a particular time, can be obtained from mass loss calorimetric results in Section 4.4.1.

**Figure 4.11:** Experimental and calculated thermal conductivity values vs. temperature of (a) M90, (b) M93 and (c) FX5002
To develop a model, this equation should be solved by a finite element method using appropriate boundary conditions, which is outside the scope of this PhD study. Hence, only very simple calculations were done and are presented here as an exemplar of what information can be gained. The thermal conductivity values, k calculated by using the above parameters at different temperatures for each intumescent coating are shown in Figure 4.11 and the detailed calculations are given in Appendix I.

For comparison of the experimental values of thermal conductivity from Section 4.5 are shown in Figure 4.11. The results show that although the calculated thermal conductivity values of all intumescent coatings are slightly lower than the experimental values, the trend is similar. In the literature, the thermal conductivity values of intumescent char material are reported to be varying from 0.1 W/mK to 0.4 W/mK from room temperature to 600°C [6,7]. The calculated thermal conductivity values are within the range as reported in the literature.

Since glass transition temperature and decomposition temperature of the epoxy resin used in these composites are ~ 180 and 250 °C, respectively, a temperature point at 200 °C was selected to evaluate the minimum requirement for both thermal conductivity and coating thickness in order to protect the underlying composite structure. The results are reported in Table 4.7.

**Table 4.7: The calculation of thermal conductivity and char thickness at 200 °C**

<table>
<thead>
<tr>
<th>Coating</th>
<th>Temp. underneath the coating (°C)</th>
<th>Char thickness (mm)</th>
<th>Cal. thermal conductivity (W/mK)</th>
<th>Exp. thermal conductivity (W/mK)</th>
</tr>
</thead>
<tbody>
<tr>
<td>M90</td>
<td>200</td>
<td>3.2</td>
<td>0.21</td>
<td>0.20</td>
</tr>
<tr>
<td>M93</td>
<td>200</td>
<td>5.1</td>
<td>0.11</td>
<td>0.18</td>
</tr>
<tr>
<td>FX5002</td>
<td>200</td>
<td>6.5</td>
<td>0.17</td>
<td>0.20</td>
</tr>
</tbody>
</table>

The evaluated thermal conductivity values and char thickness values in Table 4.7 suggest that ~ 0.2 W/mK is the minimum thermal conductivity value of an approximately 3 mm thick char that should be able to protect a composite structure from heat to maintain structural integrity for a period of time.
4.7 Conclusions

In this study, improved fire resistance of a GRE composite was demonstrated by coating with three different intumescent coatings. The cone results showed that these three coatings had no effect on the TTI of the GRE composite, but significantly reduced the peak heat release (PHRR) values (> 50%). The coatings, however, prolonged burning time of GRE composite, i.e. from 300 s for the control sample to 1000 s for the coated samples. These coatings could delay and reduce the heat transfer through the laminate, measured as delay in time to reach a surface temperature of the laminate (below the coating) of 180 °C, which is $T_g$ (glass transition temperature) of almost epoxy resins. The thermal barrier effect of these coatings increased with increasing thickness. This indicates the effectiveness of the expanded intumescent char layer on the surface to protect the underlying resin, hence helping to maintain the mechanical integrity of the composite laminates during exposure to fire/heat for a longer time. The best results were observed from 3 mm thick coatings of the epoxy based intumescent coatings and 1 mm thick coating of water based intumescent coating.

Based on these results, a target performance for the thermal barrier coatings being developed in this PhD work can be set. An ideal coating during exposure to 50 kW/m² heat flux in a cone calorimeter is expected to have following criteria.

- Prevent ignition or should increase TTI
- Reduce PHRR ≥ 50% compared to uncoated composite
- Should not prolong burning time
- Should delay the time-to-reach the surface temperature equal to softening temperature of the resin (180 °C) by more than 50%

A good correlation in the thickness of intumescent char and its thermal conductivity at evaluated temperatures has been observed. Using char thickness at a particular temperature, the temperature gradient between the surface and underneath the coating at that temperature, and porosity of the char, thermal conductivity values could be calculated using a simple heat transfer equation. There was a reasonable agreement
between calculated values with the experimental ones. This approach could be used to predict the requirements that an ideal coating should possess that would enable a composite structure to survive at a defined heat flux for a specified period of time.

4.8 References


Appendix I: The calculation of thermal conductivity values of intumescent coatings

Figure I.1: Schematic representation of an intumescent composite laminate
Table I.1: Parameters used for calculation of thermal conductivity of chars of the M90 epoxy based intumescent coating at different temperatures

<table>
<thead>
<tr>
<th>Time (s)</th>
<th>The experimental temperature profile of the coatings (°C)</th>
<th>Char expansion thickness (mm)</th>
<th>Porosity (ρc_p)</th>
<th>Cal. thermal conductivity (W/mK)</th>
</tr>
</thead>
<tbody>
<tr>
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<td>Surface</td>
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<td></td>
</tr>
<tr>
<td>1</td>
<td>50</td>
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</tr>
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<td>2.90 x10^4</td>
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<td>4.43 x10^4</td>
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<td>4.43 x10^4</td>
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<td>4.43 x10^4</td>
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<td>7.7</td>
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Table I.2: Parameters used for calculation of thermal conductivity of chars of the M93 epoxy based containing DOPO intumescent coating at different temperatures

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<th>Time (s)</th>
<th>The experimental temperature profile of the coatings (°C)</th>
<th>Char expansion thickness (mm)</th>
<th>Porosity ($\rho c_p$)</th>
<th>Cal. thermal conductivity (W/mK)</th>
</tr>
</thead>
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<td></td>
<td>Surface</td>
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<tr>
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Table I.3: Parameters used for calculation of thermal conductivity of chars of the FX5002 water based intumescent coating at different temperatures

<table>
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<th>Time (s)</th>
<th>The experimental temperature profile of the coatings (°C)</th>
<th>Char expansion thickness (mm)</th>
<th>Porosity ((\rho c_p))</th>
<th>Cal. thermal conductivity (W/mK)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Surface</td>
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<td></td>
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<tr>
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Chapter 5

NANOCLAY DEPOSITIONS

This chapter explores the combination of atmospheric-pressure cold plasma and nanotechnology to develop a thermal barrier surface coating on the GRE laminate. A commercially available organically modified layered silicate nanoclay (Cloisite 30B) was deposited on the surfaces of glass fibre-reinforced epoxy composite laminates. For this, the clay was dispersed in ethanol and the suspension was sprayed on the laminate surface using an air brush. Two approaches have been undertaken to physically/chemically bind the clay with the resin: 1) an atmospheric argon plasma was used in the presence and absence of a silicon-containing monomer and 2) a phenolic resin was used as a binder. The surface morphology of each nanoclay coated surface was studied by SEM, IR-ATR and a water drop test. The thermal barrier properties of these coatings have been studied using a cone calorimeter. The durability of the coatings to peeling and water absorption has been also studied.

5.1 Physical properties of the coatings

The thickness of each coating was measured using a digital caliper, and clay deposition (wt%) was calculated as discussed in Section 3.3.2.4 (Chapter 3). The results are given in Table 5.1. As can be seen in Table 5.1, a 310 µm thick coating (30B/Ar coating) could be obtained with the Ar-plasma. The % clay deposited was 3.66 % on the GRE laminates. With Ar-HMDSO plasma, a 320 µm thick coating was obtained, the coating (30B/HMDSO coating) has, however, clay and the HMDSO monomer. The % clay deposition of the 30B/HMDSO coating was calculated by equation (1) in Section 3.3.2
(Chapter 3), to be 3.19%. The 30B/Phe coating, containing 10 wt% phenolic binder, was of 380 µm thickness with 4.53% clay deposited. On comparing these coatings, it can be observed that the use of a phenolic binder allows for greater concentration of nanoclay particles to be formed on the GRE laminate surface. Moreover, the use of HMDSO monomer in the Ar-plasma did not contribute to an improvement in the concentration of nanoclay deposition when compared to the use of the normal Ar-plasma surface activation.

Table 5.1: Physical properties of the coatings, referring to the amount applied on a 75 mm x 75 mm plaque of the GRE laminates

<table>
<thead>
<tr>
<th>Sample</th>
<th>Nanoclay coating</th>
<th>Coating thickness (µm)</th>
<th>Mass of coating (g)</th>
<th>Mass of clay in coating (g)</th>
<th>Clay deposition (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>GRE-30B/Ar</td>
<td>30B/Ar</td>
<td>310 ± 50</td>
<td>0.768 ± 0.163</td>
<td>0.768 ± 0.163</td>
<td>3.66 ± 0.78</td>
</tr>
<tr>
<td>GRE-30B/HMDSO</td>
<td>30B/HMDSO</td>
<td>320 ± 50</td>
<td>0.618 ± 0.024</td>
<td>0.616 ± 0.024</td>
<td>3.19 ± 0.07</td>
</tr>
<tr>
<td>GRE-30B/Phe</td>
<td>30B/Phe</td>
<td>380 ± 70</td>
<td>1.057 ± 0.049</td>
<td>0.951 ± 0.044</td>
<td>4.53 ± 0.22</td>
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</tbody>
</table>

Note: 30B/Ar coating: Ar-plasma → 30B clay deposition using LbL → Ar-plasma 30B/HMDSO coating: Ar/HMDSO plasma → 30B clay deposition using LbL → Ar-plasma 30B/Phe: 30B/Phenolic resin blend deposition using LbL → curing at RT, 24 h and post curing at 80°C, 24 h

5.2 Surface characterisation

5.2.1 Effect of plasma on the epoxy surface

5.2.1.1 Water drop test

A simple water drop test was used to study the effect of plasma treatment on the surface of the GRE composite laminates (see Section 3.6.3 (Chapter 3)). The results at 0, 1, 60 and 120 s are shown below in Figure 5.1.
The results show that when a drop of water is placed on the GRE laminate (control) only the water droplet remains as a droplets and a hydrophobic surface is observed, see Figure 5.1 (control). Even after 120 s, the control GRE laminate retains the hydrophobic surface property. In the case of the Ar-plasma-treated sample, a water drop test was applied directly following plasma exposure. The water drop spreads as soon as being dropped on the surface, indicating complete wetting and that the surface is super hydrophilic. This is likely due to the Ar-plasma treatment activating and creating polar groups on the GRE laminate surface, which would be expected to increase the hydrophilicity of the surface [1]. For the Ar/HMDSO plasma treated sample, the water drop remains on the surface until 120 s. The nature of the surface from the behaviour of the water drop can be identified as non-wetting and hydrophobic. This indicates that the GRE substrate surface became highly hydrophobic after the polymerised HMDSO formed a film on the surface.

5.2.2 Effect of plasma and phenolic binder on nanoclay deposition

5.2.2.1 Infrared spectroscopy (IR) of the surfaces

To support the water drop results and to observe the effect of the plasma on the surface, treated with Ar/HMDSO plasma, the surface was characterised by IR-ATR. The transmittance IR spectra of treated laminate and control laminates are shown in Figure 5.1.
5.2. The IR spectra of the Cloisite 30B nanoclay and the three surface-coated laminates are shown in Figure 5.3.

Figure 5.2: IR spectra of (a) control, (b) Ar/HMDSO plasma treated GRE laminates

Figure 5.3: IR spectra of (a) Cloisite 30B, (b) GRE-30B/Ar, (c) GRE-30B/HMDSO and (d) GRE-30B/Phe
In Figure 5.2, it can be seen that the characteristics peaks of epoxy resin appear to have decreased and overlaid by peaks arising from the Ar-HMDSO plasma deposited film. The peaks due to aromatic C-H (1606 and 1509 cm\(^{-1}\)) and aromatic ring stretching (1583 and 1450 cm\(^{-1}\)) decreased in intensity, the broad peak at 3400 cm\(^{-1}\) (O-H stretching) and the peaks at 2925 and 2852 cm\(^{-1}\) due to -CH\(_2\)- and -CH\(_3\) stretching have nearly disappeared. The peaks at 1110 and 1080 cm\(^{-1}\) of C-O and 1241 cm\(^{-1}\) of epoxy ring overlaid by new peaks at 1035 and 1065 cm\(^{-1}\), which can be attributed to Si-O-Si and Si-O-C bonds, respectively [2,3,4]. These observations indicate that the polymerisation of HMDSO on the GRE composite surface has occurred.

In Figure 5.3 (a), the characteristic peaks of Cloisite 30B can be identified as: 3626 cm\(^{-1}\) (non-hydrogen-bonded O-H stretching) [5], 3400-3200 cm\(^{-1}\) (hydrogen-bonded O-H stretching and N-H stretching) [6], 1006 cm\(^{-1}\) (Si-O-Si stretching), and the group of peaks at 2922, 2846 and 1465 cm\(^{-1}\) (C-H stretching and bending) due to the methylene group of the organic modifier of the clay [7,8,9]. As clearly seen in Figure 5.3 (b, c, and d), all of the Cloisite 30B peaks are also present in GRE-30B/Ar, GRE-30B/HMDSO and GRE-30B/Phe samples. In all the coated samples, however, a new peak at 1218 cm\(^{-1}\) appeared, which can be assigned to the stretching of C-O and C-N bonds in the alkyl ammonium ion of the organic modifier group of Cloisite 30B nanoclay (see Figure 5.3). The absence of the peak at 1218 cm\(^{-1}\) in spectra of the Cloisite 30B clay could be explained on the basis that the clay has been tested as a powder where clay platelets are stacked together, whereas when it is dispersed in ethanol under shear (prior to coating on the surface of the laminate), the exfoliation of the platelets occurs and hence, and the organic modifier is relatively more exposed on the surface. On the other hand, in the GRE-30B/Phe sample, reduction in intensity of the peaks in the region of 2925 - 2852 cm\(^{-1}\) (-CH\(_2\)- and -CH\(_3\) stretching), 3628 cm\(^{-1}\) (non-hydrogen-bonded O-H stretching) and 1006 cm\(^{-1}\) (Si-O-Si stretching) indicates the masking of surface by the phenolic resin. Furthermore, new additional peaks occur which are characteristic of a phenolic structure, such as at 1372 cm\(^{-1}\) due to O-H bonds of the phenolic groups and at 1653, 1611 and 1512 cm\(^{-1}\) due to the C=C in the phenolic rings [10].
5.2.2.2 Scanning electron microscopy (SEM)

To support the FTIR results, changes in laminate surface morphology were studied using SEM. Their SEM images are shown in Figure 5.4.

Figure 5.4: SEM images of the GRE control, Ar/HMDSO plasma-treated laminate, GRE-30B/Ar, GRE-30B/HMDSO and GRE-30B/Phe samples at various magnifications
The images show that the surface of the control sample is smooth (Figure 5.4 a - c). The effect of Ar-HMDSO plasma treatment can be observed from Figure 5.4 (d-f) where a layer of the polymerised HMDSO can be clearly seen. As compared to control sample, the surfaces of the nanoclay coated samples GRE-30B/Ar and GRE-30B/HMDSO are completely different, becoming rougher and scalier due to the nanoclay concentrating on the surface, as seen in Figure 5.4 (g - l). The surface of GRE-30B/Phe on the other hand is smooth and more uniform, see Figure 5.4 (m - o). This indicates that the use of the phenolic resin helps in binding the nanoclay particles more uniformly onto the laminate substrate.

5.3 Mechanism of nanoclay deposition using Ar-plasma treatments

Based on the IR and SEM results discussed above, the possible mechanism of nanoclay deposition on the plasma treated surface of glass fibre-reinforced epoxy (GRE) composites can be proposed to be as shown in Figure 5.5.

![Diagram showing possible mechanism of nanoclay deposition on glass fibre-reinforced epoxy (GRE) composite by using an Ar-plasma.]

**Figure 5.5:** Possible mechanisms of the nanoclay deposition on glass fibre-reinforced epoxy (GRE) composite by using an Ar-plasma
The surface of epoxy composite laminate normally consists of carbon, oxygen and hydrogen. Ar-plasma treatment can create O-functional groups such as hydroxyl (-OH), carbonyl (C=O), peroxyl (O-O) and carboxylic (O=C-OH) groups on the polymeric surface [11,12,13] as shown in Figure 5.5. The plasma has enough energy to break covalent bonds to produce free radicals or subtract hydrogen to produce a negative charge on the surface. These active species can then react with the alkyl ammonium ion in the 30B nanoclay structure. Reaction of alkyl ammonium ion with a laminate surface may be partly an ionic interaction via carboxylic acid species (see Figure 5.6 (a) and/or a radical grafting reaction between alkyl group of such ions and of the surface, using O – O groups as initiating sites (see Figure 5.6 (b)).

Figure 5.6: Possible reactions of alkyl ammonium ions with an epoxy surface: a) ionic interaction and b) radical grafting
A possible mechanism for nanoclay coating deposition in the presence of an Ar-HMDSO plasma treatment (30B/HMDSO coating), is shown in Figure 5.7. With the Ar-HMDSO plasma, all the HMDSO monomer molecules become extensively fragmented in the powerful plasma, most often into single atoms. This is followed by first order recombination to produce a new molecular structure \[14\]. These free radicals, and radical-sites from the HMDSO monomer produced in the plasma might randomly react with radical sites formed on the GRE surface to form crosslinks via its oxygen atoms or with silane groups through the -O-Si bond [3,15], resulting in the thin film of polymerised HMDSO. Generally, the functionalities of siloxane oligomers and polysiloxanes include silanol, chlorosilyl, hydrosilyl, vinyl, and allyl groups [16,17]. When nanoclay particulates are sprayed on the polymerised HMDSO layer, the functionalities of the polymerised HMDSO react with the alkyl ammonium ion in the 30B nanoclay structure and some covalent bonds are formed as shown in Figure 5.7.

![Figure 5.7: Possible mechanisms of the nanoclay deposition on GRE composite by using an atmospheric Ar/HMDSO-plasma and an Ar-plasma](image_url)
5.4 Flammability behaviour of GRE composites with nanoclay depositions

As seen from Table 5.1, the nanoclay coating thickness is only 310-380 µm, which is too thin to provide effective thermal barrier effect to the laminate exposed to 50 kW/m² in a cone calorimeter. Hence, 35 kW/m² heat flux without a spark ignition source was chosen. The HRR vs. time curves of all samples are shown in Figure 5.8. The analysed results are given in Table 5.2, including time-to-ignition (TTI), peak heat release rate (PHRR), Time-to-PHRR (T<sub>PHRR</sub>), total heat release (THR) and fire growth index (FIGRA).

Table 5.2: Cone calorimetric data for the control and all coated samples at 35 kW/m² heat flux without an ignition source

<table>
<thead>
<tr>
<th>Samples</th>
<th>Specimen No.</th>
<th>% clay deposition</th>
<th>TTI (s)</th>
<th>PHRR (kW/m²)</th>
<th>T&lt;sub&gt;PHRR&lt;/sub&gt; (s)</th>
<th>THR (MJ/m²)</th>
<th>FIGRA (kW/m²s)</th>
</tr>
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<tbody>
<tr>
<td>Control</td>
<td>1, 2, 3</td>
<td>-</td>
<td>97 ±4</td>
<td>526 ±17</td>
<td>127 ±1</td>
<td>33.8 ±4.0</td>
<td>4.1 ±0.1</td>
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<tr>
<td>GRE-30B/Ar</td>
<td>1</td>
<td>4.23</td>
<td>174</td>
<td>400</td>
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<td>28.2</td>
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<td>2T, 3T</td>
<td>3.13 ±0.14</td>
<td>100 ±2</td>
<td>443 ±16</td>
<td>162 ±14</td>
<td>48.4 ±3.2</td>
<td>2.8 ±0.3</td>
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<tr>
<td>GRE-30B/HMDSO</td>
<td>1</td>
<td>3.10</td>
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<td>44.3</td>
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<td>2T, 3T</td>
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<td>136 ±1</td>
<td>480 ±21</td>
<td>184 ±4</td>
<td>45.0 ±1.1</td>
<td>2.6 ±0.1</td>
</tr>
<tr>
<td>GRE-30B/Phe</td>
<td>1, 2T</td>
<td>4.12 ±0.05</td>
<td>99 ±7</td>
<td>410 ±9</td>
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<td>-</td>
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<td>1.3</td>
<td>0.03</td>
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</table>

Note: * indicates that the sample did not ignite; Samples denoted as T represent those in which thermocouples were inserted; FIGRA is the fire growth rate index, defined as the ratio of PHRR and the time at which PHRR occurs.

The heat release (HRR) curve in Figure 5.8 shows that the control sample without any surface coating ignited after 97 s of continuous radiant heat exposure, after which period the heat release values rose reaching a peak heat release rate value (PHRR) of 526 kW/m² at 119 s. The process of burning was finished within 281 s with 33.8 MJ/m² the total heat release rate (THR). At the end of the experiment, all the resin had been burnt and no residual char was left to hold the glass fabric layers together (see Figure 5.9 (a)).
Figure 5.8: HRR versus time curves of the control GRE and a) GRE-30B/Ar, b) GRE-30B/HMDSO and c) GRE-30B/Phe samples and d) mass loss versus time curves of all samples on cone exposure at 35 kW/m$^2$ heat flux without an ignition source [* indicates that the sample did not ignite]
In Table 5.2, it can be seen that the GRE nanoclay coated samples show variable results depending upon the clay concentration on the surface. For the GRE-30B/Ar sample surface coated with nanoclay using the Ar-plasma, the two specimens with 3.13 wt% clay deposition ignited at 100 s, the PHRR, however, is reduced compared to the control sample and the time-to-PHRR ($T_{PHRR}$) is delayed. The HRR curves for those two GRE-30B/Ar specimens (2 and 3) are broader than that of the control sample (Figure 5.8 (a)), resulting in a higher total heat release (THR). For another one specimen, with 4.23 % clay deposition (specimen 1), the TTI is considerably increased to 174 s, PHRR to 400 kW/m² and $T_{PHRR}$ to 194 s. The THR value was reduced to 28.2 MJ/m². The reduction in PHRR and increase in $T_{PHRR}$ in all GRE-30B/Ar samples also results in reducing the fire growth index values, FIGRA (PHRR/$T_{PHRR}$). The FIGRA can be used to assess the materials in term of potential fire safety [18]. The FIGRA in GRE-30B/Ar is reduced by 32% and suggests that the nanoclay has an effect in reducing the fire risk. These three parameters (increase in TTI, reduction in PHRR and increase in $T_{PHRR}$) are important in assessing the thermal barrier efficiency of any material, typically shown by coatings such as intumescent or ceramic coatings which provide passive fire protection [19,20,21]. At the conclusion of the cone calorimeter test, a thin layer of charred residue was left on the surface of the laminate. This being very thin and flimsy, it is not capable of retaining the integrity of the laminate by thermally protecting the underlying resinous part (Figure 5.9 (b)).

The cone results for the sample GRE-30B/HMDSO, coated with nanoclay using the Ar-HMDSO plasma, are not as good as those for GRE-30B/Ar as can be seen from Figure 5.8 (b) and Table 5.2. With 3.26 wt% clay deposition (specimens 2 and 3), the TTI and $T_{PHRR}$ are increased. The PHRR is not reduced to the same extent as in the case of GRE-30B/Ar. This is probably due to the % deposited clay on GRE-30B/HMDSO’s surface being less than that of GPE-30B/Ar, see Table 5.2. These results also show that the HMDSO polymer has no fire retardant properties and did not help in increasing the clay deposition on the surface. A very thin charred layer was observed similar to that in the case of GRE-30B/Ar at the end of the cone experiment (see Figure 5.9 (c)).
With 4.78 wt% clay deposited, the composite laminate GRE-30B/Phe containing nanoclay and polymerisable phenolic binder did not ignite. However, it did ignite with lower clay depositions (specimens 1 and 2). The HRR curves of GRE-30B/Phe samples are significantly different than all the other samples as can be seen from Figure 5.8 (a-c). With respect to the control sample, the TTI and $T_{\text{PHRR}}$ of GRE-30B/Phe have barely increased, but the PHRR decreased from 526 to 410 kW/m$^2$ and FIGRA decreased by 27% without significantly increasing the THR value. In the GRE-30B/Phe coating, the phenolic resin binder is exposed on the surface, which ignites easily and hence, the TTI is little affected. The reduction in PHRR and FIGRA values without significantly increasing burning time are due to the inherently flame retardant character of the phenolic resin. The char residue at the end of the experiment was similar to the other coatings as seen in Figure 5.9 (d). The nanoclay content on the surface is also higher in this sample compared to other samples (see Table 5.2).

As discussed in Section 3.7.3 (Chapter 3), mass loss during cone experiments could only be recorded for the first specimen of all the samples and the results are shown in Figure 5.8 (d). In the other two specimens in which thermocouples were embedded, the thermocouple wires upset the mass balance, making it very difficult to accurately record the mass. The results in Figure 5.8 (d) show that the GRE-30B/Ar1 significantly retarded the mass loss rate when compared to the control, whereas, the mass loss curves of GRE-30B/HMDSO1 and GREC1 are not very different to that of the control. This is due to the high concentration of clay in GRE-30B/Ar1, which is enough to provide the thermal barrier effect. This observation is also consistent with the cone results in Table 5.2, showing that GRE-30B/Ar1 showed the best fire resistance property compared to GRE-30B/HMDSO1 and GRE-30B/Phe1.

![Figure 5.9: Digital images of the charred residues of (a) control, (b) GRE-30B/Ar, (c) GRE-30B/HMDSO and (d) GRE-30B/Phe at the end of the cone calorimeter experiments](image)
From the cone results of these three coated samples, it can be concluded that GRE laminates which were surface coated by nanoclays using the Ar-plasma or the Ar-HMDSO plasma or the phenolic binder gave variable results depending upon the concentration of clay on the substrate and whether the nanoclay completely covered the surface or some of the resin was exposed. If the surface is completely covered by a high concentration of clay, it is expected that the clay will act as a barrier. This is indicated by the delay in TTI or time-to-PHRR and even if the sample was not ignited. If, however, some resin is exposed on the surface, the resin will ignite and the barrier effect of the nanoclay will not be efficient.

5.5 Thermal barrier effect of the nanoclay depositions

The thermal barrier effect of these coatings was evaluated using the temperature profiles of the surface ($T_S$) and the back surface (unexposed) ($T_B$) of the laminate. These were recorded via the $K$-type thermocouples as mentioned in Section 3.7.3 (Chapter 3). The temperature profiles at the back surface ($T_B$) of all the GRE composite samples are plotted in Figure 5.10.

![Figure 5.10: The back surface temperature ($T_B$) as a function of time for the control and all nanoclay coated samples at 35 kW/m$^2$ heat flux. (*) indicates the sample did not ignite]
The extracted numerical data from both temperature profiles in terms of times to reach 180 and 250 °C are also reported in Table 5.3. These temperatures were selected because they represent the glass transition and decomposition temperatures of the epoxy resin, respectively.

Table 5.3: The time required to reach the selected temperatures at the surface and back surface of all samples at 35 kW/m$^2$ without an ignition source

<table>
<thead>
<tr>
<th>Sample</th>
<th>% Clay deposition</th>
<th>Time (s) to reach 180 °C</th>
<th>Time (s) to reach 250 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Surface</td>
<td>Back surface</td>
</tr>
<tr>
<td>Control</td>
<td>-</td>
<td>18 ± 5</td>
<td>40 ± 7</td>
</tr>
<tr>
<td>GRE-30B/Ar</td>
<td>3.13 ±0.14</td>
<td>16 ± 1</td>
<td>44 ± 3</td>
</tr>
<tr>
<td>GRE-30B/HMDSO</td>
<td>3.26 ±0.02</td>
<td>18 ± 7</td>
<td>48 ± 3</td>
</tr>
<tr>
<td>GRE-30B/Phe3*</td>
<td>4.78</td>
<td>18 ± 1</td>
<td>52 ± 2</td>
</tr>
</tbody>
</table>

Note: * indicates that the sample did not ignite; [+ ] indicates an increase in Δt with respect to the control

The temperature profiles in Figure 5.10 show that the GRE-30B/Phe samples had a slower temperature rise at the back surface after 120 s when compared to that of the control sample. However, the difference in temperature rise between those of the GRE-30B/Ar and GRE-30B/HMDSO samples and the control samples is less. This is because GRE-30B/Phe2 and GRE-30B/Phe3 had a higher concentration of clay compared to GRE-30B/Ar2, GRE-30B/Ar3, GRE-30B/HMDSO2 and GRE-30B/HMDSO3 (see Table 5.3).

To compare the thermal barrier efficiency of each coating, the time required for the back surface to reach 180 and 250 °C of all the samples at 35 kW/m$^2$ heat flux are tabulated in Table 5.3. For the samples GRE-30B/Ar and GRE-30B/HMDSO, the time required to both temperature points is not much different than the control sample, whereas, for the GRE-30B/Phe, the delay before the back surface temperature reaches 180 and 250 °C is increased by ~12 s compared to the control sample. These observations indicate that in the Ar-plasma coated nanoclay sample, the silicate layer on the charred surface is not
thick enough to effectively delay the heat transfer through the sample. If a high concentration of nanoclay is used with an inherently flame retardant resin, the thermal barrier efficiency can be improved.

5.6 Durability of coatings

5.6.1 Effect of water on nanoclay depositions

5.6.1.1 Wettability

The water drop test was employed to evaluate the wettability of the nanoclay coatings similarly to that used in Section 5.2.1.1. The results at 0, 1, 60 and 120 s are shown in Table 5.4.

Table 5.4: Surface wettability of different nanoclay coated GRE laminates at various times

<table>
<thead>
<tr>
<th>Times</th>
<th>GRE-30B/Ar</th>
<th>GRE-30B/HMDSO</th>
<th>GRE-30B/Phe</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 s</td>
<td><img src="image1.png" alt="Image" /></td>
<td><img src="image2.png" alt="Image" /></td>
<td><img src="image3.png" alt="Image" /></td>
</tr>
<tr>
<td>1 s</td>
<td><img src="image4.png" alt="Image" /></td>
<td><img src="image5.png" alt="Image" /></td>
<td><img src="image6.png" alt="Image" /></td>
</tr>
<tr>
<td>10 s</td>
<td><img src="image7.png" alt="Image" /></td>
<td><img src="image8.png" alt="Image" /></td>
<td><img src="image9.png" alt="Image" /></td>
</tr>
<tr>
<td>60 s</td>
<td><img src="image10.png" alt="Image" /></td>
<td><img src="image11.png" alt="Image" /></td>
<td><img src="image12.png" alt="Image" /></td>
</tr>
<tr>
<td>120 s</td>
<td><img src="image13.png" alt="Image" /></td>
<td><img src="image14.png" alt="Image" /></td>
<td><img src="image15.png" alt="Image" /></td>
</tr>
</tbody>
</table>

Table 5.4, the GRE-30B/Ar shows high wettability of the coating surface. After 1 s, the water drop flattened and started to spread by surface wetting, followed by growth of the water spot up to 60 s. This indicates that the surface, after nanoclay treatment, has significantly increased wettability as comparing with uncoated sample, see Figure 5.1
With polymerised HMDSO, the GRE-30B/HMDSO shows a greater surface wettability than GRE-30B/Ar. For GRE-30B/Phe, the use of phenolic resin binder produces the lowest surface wettability compared to the other two samples.

5.6.1.2 Durability of coatings after immersion in water

The effect of water on the durability of three different nanoclay coatings was investigated using the water-soak test (for details see Section 3.9.1, Chapter 3). The results of water durability have been measured in terms of weight change after water soaking. The digital images and % weight change results are given in Table 5.5.

Table 5.5: The digital images of all GRE surfaces before and after the water-soak test, and weight loss (wt%) after the test

<table>
<thead>
<tr>
<th>Sample</th>
<th>Images</th>
<th>% Weight loss after 24 h soaking in water and 24 h drying at RT</th>
<th>% Weight loss after drying at RT</th>
<th>% Weight loss after drying at 100°C for 2h</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>-</td>
<td>-</td>
<td>-0.03 ±0.01</td>
<td>-0.10 ±0.07</td>
</tr>
<tr>
<td>GRE-30B/Ar</td>
<td></td>
<td>-</td>
<td>-0.75 ±0.20</td>
<td>-0.90 ±0.04</td>
</tr>
<tr>
<td>GRE-30B/HMDSO</td>
<td></td>
<td>-</td>
<td>-18.1 ±0.35</td>
<td>-28.7 ±1.16</td>
</tr>
<tr>
<td>GRE-30B/Phe</td>
<td></td>
<td>-</td>
<td>-0.05 ±0.03</td>
<td>-0.06 ±0.09</td>
</tr>
</tbody>
</table>
The results in Table 5.5 show that GRE-30B/Ar sample after soaking in water for 24 h had minimal weight loss of 0.75%, even after drying in an oven at 100 °C, indicating that there is no significant loss of clay. This weight change value is similar to that for the control sample. In the digital image of the surface of the GRE-30B/Ar sample after the water soak test, small cracks appeared on the surface. This indicates that the water penetration through the coating layer causes damage to the coating. With the Ar-HMDSO treatment, GRE-30B/HMDSO shows the highest % weight loss (18.1%), increasing further to 28.7 % after drying at 100 °C. This indicates that the coating adsorbed water, which was desorbed during drying. The damage to the coating can be clearly seen in Table 5.5, suggesting that this coating is not firmly bonded to the surface due to the extra layer of polymerised HMDSO film. This can be related to the structure of the coating in Figure 5.7, where electrostatic interactions are less than those for the coating shown in Figure 5.5. Hence, this coating is more hydrophilic and shows worst performance in the water-soak test. GRE-30B/Phe, shows the lowest % weight lost after soaking in water compared to other two coated samples and also no damage was observed from the image in Table 5.5. This indicates that the use of the phenolic resin binder produces the most stable coating with regard the effect of water and moisture. Thus, the performance of each coating in terms of its durability can be ranked from best to worst as 30B/Phe coating>30B/Ar coating>30B/HMDSO coating.

5.6.2 Adhesion between coatings and GRE surfaces

The adhesion between these three different nanoclay coatings and the GRE composite was studied using the tape pull test (Section 3.9.2, Chapter 3). Table 5.6 shows the loss in weight and % coating peeled off after the tape test at 180° pulling angle for all the coated samples. Digital images of all the tapes after test were taken and also shown in Table 5.6. The results show that the GRE-30B/Ar surface had less than 1% weight loss and only 1.5 wt% clay peeled off after the tape pull tests, mainly from the third area as seen in the image of GRE-30B/Ar in Table 5.6. This indicates non-uniformity of plasma treatment leading to varied bonding strength between the nanoclay particles and different areas of the surface of the GRE laminate.
Table 5.6: The changes in weight and peeling of the coatings after the tape pull test from different areas of the coated samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>% Coating deposition</th>
<th>Images of the tapes after the tape pull test</th>
<th>% Total weight loss</th>
<th>% Peeling of the coating</th>
</tr>
</thead>
<tbody>
<tr>
<td>GRE-30B/Ar</td>
<td>3.3</td>
<td><img src="image1" alt="Images" /></td>
<td>0.05 ±0.02</td>
<td>1.5</td>
</tr>
<tr>
<td>GRE-30B/HMDSO</td>
<td>3.1</td>
<td><img src="image2" alt="Images" /></td>
<td>0.12 ±0.01</td>
<td>3.9</td>
</tr>
<tr>
<td>GRE-30B/Phe</td>
<td>4.4</td>
<td><img src="image3" alt="Images" /></td>
<td>0.01 ±0.01</td>
<td>0.1</td>
</tr>
</tbody>
</table>

The Ar-HMDSO-treated sample, GRE-30B/HMDSO, shows the highest % clay peeling off (3.9 wt%), and the peeling of the clay from the three different areas is very similar. This may be due to the nanoclay particles being bonded onto the polymerised HMDSO instead of the surface of laminate. Thus, the bond is weakened and it easily peeled off. The peeling of 30B/Phe coating in GRE-30B/Phe, containing phenolic resin as binder, is minimal, which shows that, during curing, the phenolic resin completely embeds the nanoclay. These observed results suggest that a stable coating can be obtained using the atmospheric argon plasma treatment or using a phenolic resin binder.
5.7 Conclusions

This work has shown that the nanoclays can be uniformly deposited on the surface of glass fibre-reinforced epoxy composites by dispersing in a solvent and spraying by an air brush. The use of an Ar-plasma treatment to deposit the nanoclay can achieve a ~3 wt% loading of nanoclay upon a GRE composite surface, while the presence of HMDSO monomer in Ar-plasma does not contribute to an improvement in the concentration of nanoclay compared to a neat Ar-plasma treatment. In comparison, the use of a phenolic binder increases the loading of clay to ~4 wt%. By pre-treating the laminate surface with an argon plasma, nanoclays are bonded to the epoxy surface and the coating does not peel off when tested by the tape pull method. With the Ar-HMDSO plasma, the adhesion between the coating and the laminate surface was slightly less than that from Ar-plasma, due to the clay being bonded to the silicone polymer. On the other hand, the phenolic resin binder polymerises on the epoxy surface and becomes chemically bonded thus providing better adhesion than either of the aforementioned coatings. After 24 h of ageing in water, the Ar-plasma-treated and phenolic resin binder-containing samples showed minimal weight change, indicating the durability of the coatings. The Ar-HMDSO plasma-treated coating, however, was sensitive to water and showed maximum damage. While the Ar-plasma-treated coating showed less signs of cracking, the Ar-HMDSO-treated coating was badly damaged. In terms of thermal barrier properties, the best results were shown by the Ar-plasma-treated coating, while the phenolic resin-containing coating could effectively reduce the PHRR. It is worth pointing out that the thermal barrier effect of the nanoclay coating is strongly dependent on the concentration of clay on the substrate and whether it completely covers the surface or resin present on the surface is exposed directly to the heat. In future work other methods of clay deposition will be explored. Another important conclusion is that the presence of HMDSO monomer does not contribute to an improvement in the concentration of nanoclay deposition on the surface or provide improved thermal barrier properties to the laminate.
5.8 References


CERAMIC PARTICLE COATINGS

In this chapter, five commercially available ceramic nano and micro particles have been used as thermal barriers on glass fibre-reinforced epoxy composites. The coatings have been prepared by dispersing 70 wt% ceramic powder in 30 wt% flame retarded epoxy resin or a phenolic resin. Coatings were applied by a roller and paint brush to obtain the required thicknesses. This chapter has been divided in three parts. In Part I, a flame retarded epoxy binder has been used in the coatings and the effects of different heat fluxes on the flammability and thermal barrier efficiency of these coatings have been studied. In Part II, the flammability behaviour of different resins has been studied, which indicated that the phenolic resin was the most efficient in terms of delaying the time-to-ignition. In the final part (Part III), a phenolic resin has been used as the binder. Two sets of samples were prepared using two different approaches; a) ceramic particle with resin binder and b) ceramic particle coating with extra ceramic particles deposited on the surface.

The surface morphology of each ceramic coated surface was studied by SEM. The flammability and flame retardant properties of all samples have been studied while the durability of the coatings to peeling, impact, flexural tension and water absorption has been studied for the Part III samples only.
6.1 Part I: Ceramic particle coatings using a modified epoxy resin

Three commercially available ceramic powders (Ceepree, Recoxit and zirconia) and a flame retarded epoxy resin binder (containing 10 wt% DOPO) have been used to prepare the ceramic particle coatings, which were applied on the glass fibre-reinforced epoxy (GRE) composites by the paint brush/roller techniques as discussed in Section 3.4.2.1, Chapter 3. In this part, the surface morphology of each ceramic coated surface was studied by SEM. The flammability and thermal barrier efficiency of the coatings on the composites have been studied using a cone calorimeter at different heat fluxes.

6.1.1 Physical properties of the coatings

The variations in mass, thickness and ceramic particle deposition (wt%) of each ceramic particle coating on the GRE composite are given in Table 6.1. With different ceramic particles, 890 to 1090 µm thick coatings 34-58 % particles could be deposited on the surface of the GRE laminates.

Table 6.1: Physical properties of the ceramic particle coatings using a flame retarded epoxy resin binder applied on a 35 mm x 75 mm plaque of the GRE laminates

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ceramic:Resin ratio in coating</th>
<th>Ceramic particle and size (µm)</th>
<th>Coating thickness (µm)</th>
<th>Mass of coating (g)</th>
<th>Ceramic particle deposited (wt%, w.r.t laminate)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GRE-DP/Ce</td>
<td>70:30</td>
<td>Ceepree (&lt; 50)</td>
<td>1090 ± 70</td>
<td>4.30 ± 0.17</td>
<td>35 ± 2</td>
</tr>
<tr>
<td>GRE-DP/Re</td>
<td>70:30</td>
<td>Recoxit (&lt; 40)</td>
<td>890 ± 60</td>
<td>4.22 ± 0.04</td>
<td>34 ± 1</td>
</tr>
<tr>
<td>GRE-DP/Zr</td>
<td>70:30</td>
<td>Zirconia (&lt; 60)</td>
<td>940 ± 210</td>
<td>4.78 ± 0.21</td>
<td>38 ± 3</td>
</tr>
</tbody>
</table>

6.1.2 Surface characterisation

SEM characterisations of the surfaces of samples coated with ceramic particles are shown in Figure 6.1.
Figure 6.1 SEM images of (a) GRE-DP/Ce, GRE-DP/Re and GRE-DP/Zr surfaces, and (b) Ceepree (Ce), Recoxit (Re) and Zirconia (Zr) particles.

The results show that the particles are well dispersed in the resin coatings, i.e. there are no aggregates. The distribution of particles depends on the particle size of each ceramic type. As seen from Table 6.1 and Figure 6.1, the particle size of Recoxit is smaller (~ 40 µm) compared to Ceepree (~ 50 µm) and zirconia (~ 60 µm), which results in better particle distribution in the coating of GRE-DP/Re than GRE-DP/Ce and GRE-DP/Zr. However, the ceramic particles do not completely cover the surfaces for these three coated samples, which is probably due to the coating application method, i.e. using paint brush/roller techniques allows a good distribution of the particles on the GRE laminate surfaces, although some resin binder is exposed on the surface.
### 6.1.3 Flammability behaviour of GRE composites with ceramic particle coatings using a flame retarded epoxy binder

The flammability properties of the GRE composites without/with surface coatings were evaluated at different heat fluxes (20, 30, 40 and 50 kW/m²) using a cone calorimeter in the presence of an ignition source. The HRR curves as a function of exposure time at different heat fluxes are shown in Figure 6.2 and all derived results are presented in Table 6.2.

**Table 6.2: Cone results for different ceramic coatings on GRE composite samples exposed to 20, 30, 40 and 50 kW/m² heat fluxes with an ignition source.**

<table>
<thead>
<tr>
<th>Heat flux (kW/m²)</th>
<th>Sample</th>
<th>% Ceramic deposition</th>
<th>TTI (s)</th>
<th>PHRR (kW/m²)</th>
<th>TₚHRR (s)</th>
<th>THR (MJ/m²)</th>
<th>FIGRA (kW/m²·s)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Control</td>
<td>-</td>
<td>118 ±1</td>
<td>538 ±39</td>
<td>142 ±2</td>
<td>26.5 ±2.5</td>
<td>3.8 ±0.3</td>
</tr>
<tr>
<td>20</td>
<td>GRE-DP/Ce</td>
<td>32.7 ±0.3</td>
<td>122 ±6</td>
<td>481 ±15</td>
<td>170 ±8</td>
<td>38.0 ±0.6</td>
<td>2.8 ±0.1</td>
</tr>
<tr>
<td></td>
<td>GRE-DP/Re</td>
<td>36.8 ±0.8</td>
<td>140 ±2</td>
<td>447 ±20</td>
<td>179 ±7</td>
<td>37.3 ±3.2</td>
<td>2.5 ±0.2</td>
</tr>
<tr>
<td></td>
<td>GRE-DP/Zr</td>
<td>34.9 ±0.3</td>
<td>123 ±4</td>
<td>463 ±27</td>
<td>174 ±4</td>
<td>41.0 ±2.7</td>
<td>2.3 ±0.3</td>
</tr>
<tr>
<td></td>
<td>Control</td>
<td>-</td>
<td>62 ±1</td>
<td>571 ±14</td>
<td>83 ±3</td>
<td>30.8 ±2.4</td>
<td>6.8 ±0.5</td>
</tr>
<tr>
<td>30</td>
<td>GRE-DP/Ce</td>
<td>32.7 ±1.3</td>
<td>55 ±4</td>
<td>501 ±14</td>
<td>108 ±10</td>
<td>38.7 ±1.1</td>
<td>4.7 ±0.6</td>
</tr>
<tr>
<td></td>
<td>GRE-DP/Re</td>
<td>35.9 ±0.5</td>
<td>68 ±8</td>
<td>458 ±11</td>
<td>119 ±7</td>
<td>40.2 ±1.9</td>
<td>3.9 ±0.3</td>
</tr>
<tr>
<td></td>
<td>GRE-DP/Zr</td>
<td>36.9 ±1.5</td>
<td>61 ±7</td>
<td>470 ±2</td>
<td>121 ±7</td>
<td>40.1 ±1.5</td>
<td>3.9 ±0.2</td>
</tr>
<tr>
<td></td>
<td>Control</td>
<td>-</td>
<td>45 ±1</td>
<td>642 ±15</td>
<td>100 ±2</td>
<td>37.5 ±3.0</td>
<td>6.4 ±0.3</td>
</tr>
<tr>
<td>40</td>
<td>GRE-DP/Ce</td>
<td>34.7 ±0.9</td>
<td>38 ±1</td>
<td>553 ±23</td>
<td>110 ±8</td>
<td>41.4 ±0.2</td>
<td>5.0 ±0.2</td>
</tr>
<tr>
<td></td>
<td>GRE-DP/Re</td>
<td>34.4 ±0.3</td>
<td>49 ±1</td>
<td>478 ±13</td>
<td>116 ±6</td>
<td>41.6 ±0.3</td>
<td>4.1 ±0.3</td>
</tr>
<tr>
<td></td>
<td>GRE-DP/Zr</td>
<td>38.6 ±1.0</td>
<td>32 ±1</td>
<td>512 ±1</td>
<td>108 ±2</td>
<td>41.9 ±3.7</td>
<td>4.7 ±0.1</td>
</tr>
<tr>
<td></td>
<td>Control</td>
<td>-</td>
<td>31 ±1</td>
<td>695 ±53</td>
<td>90 ±1</td>
<td>38.7 ±3.0</td>
<td>7.7 ±0.6</td>
</tr>
<tr>
<td>50</td>
<td>GRE-DP/Ce</td>
<td>35.0 ±0.1</td>
<td>29 ±1</td>
<td>597 ±22</td>
<td>100 ±1</td>
<td>41.7 ±2.8</td>
<td>5.9 ±0.2</td>
</tr>
<tr>
<td></td>
<td>GRE-DP/Re</td>
<td>34.0 ±0.2</td>
<td>30 ±1</td>
<td>544 ±4</td>
<td>100 ±2</td>
<td>42.8 ±2.1</td>
<td>5.4 ±0.1</td>
</tr>
<tr>
<td></td>
<td>GRE-DP/Zr</td>
<td>40.0 ±1.6</td>
<td>24 ±1</td>
<td>511 ±49</td>
<td>114 ±4</td>
<td>43.5 ±0.5</td>
<td>4.1 ±0.6</td>
</tr>
</tbody>
</table>

**Note:** FIGRA index = PHRR/TₚHRR (kW/m²·s)
Figure 6.2: The HRR versus time curves at (a) 20, (b) 30, (c) 40 and (d) 50 kW/m² with an ignition source of the control, GRE-DP/Ce, GRE-DP/Re and GRE-DP/Zr samples.

Figure 6.3: Mass loss versus time curve of the control, GRE-DP/Ce, GRE-DP/Zr and GRE-DP/Re samples at 50 kW/m² with an ignition source.
In this section, the flammability behaviour of the GRE composites coated with different ceramic particles are discussed, firstly, at one heat flux (50 kW/m²) in order to observe the effect of the different components on the overall fire performance of the composites and secondly, at different heat fluxes in order to observe the effect of external heat energy input.

At 50 kW/m², Figure 6.2 (d) and Table 6.2 show that the control sample without any surface coating ignited after 31 s of continuous radiant heat exposure. After a period, the heat release rate rose reaching a peak heat release rate value (PHRR) of 695 kW/m² at 90 s. The process of burning was finished within 180 s with a 38.7 MJ/m² total heat release rate (THR). At the conclusion of the cone calorimeter test, the resin matrix is totally burned out and only glass fibres can be seen with no char in between in Figure 6.4 (a).

All ceramic particle coated (GRE-DP/Ce, GRE-DP/Re and GRE-DP/Zr) samples containing the DOPO flame retardant also show single peak HRR-curves as the control sample, but the intensity of the peak was less and the peak was broader, representing a lower peak heat release rate and a longer burning time. As can be seen in Table 6.2, the TTI values for all the coated samples are less than that of the control sample, which is most likely due to the resin-rich surface of the coated samples (see Figure 6.1). Although the resin binder is flame retarded, the phosphorus-based flame retardant in the binder resin decomposes earlier (< 250 °C) than the epoxy binder resin. The O=P-O bond in DOPO flame-retarded epoxy is less stable than the common C-C bond in pure epoxy [1]. This usually results in a lower TTI. However, Ceepree, Recoxit and zirconia particles in the GRE-DP/Ce, GRE-DP/Re and GRE-DP/Zr samples could reduce the PHRR values by 14-26 % and delay the T_{PHRR} values by 10-24 s compared to the control sample. This can be explained by the fact that Ceepree, Recoxit and zirconia particles have low thermal conductivity values, i.e. Ceepree = 1.8-2.0 W/mK [2]; Recoxit = 1.5-2.0 W/mK) [3]; zirconia = 1.5-2.0 W/mK [4], and so act as thermal insulators and prevent the diffusion of all the volatiles generated during combustion of the resin. Although the thermal conductivities of the particles are similar, based on the reduction in PHRR, the zirconia particles in GRE-DP/Zr (511 kW/m²) showed the best performance, followed by Recoxit in GRE-DP/Re (544 kW/m²) and Ceepree in GRE-DP/Ce (597 kW/m²). This is probably
due to the highest percentage of particle deposited is in GRE-DP/Zr (40%) compared to other two coated samples (see Table 6.2). The results of TTI, PHRR and T_{PHRR} of these coatings are consistent with the mass loss results in Figure 6.3, where it can be seen that all the coatings retard the mass loss rate. However, the mass loss starts at an earlier time than the control sample due to the presence of DOPO in the resin binder of the coating, which starts decomposing earlier than the unmodified epoxy resin as explained above. GRE-DP/Zr gave the most reduction in mass loss rate compared to other two coated samples. The fire growth rate index (FIGRA), the ratio of PHRR and time to PHRR, is often used to measure the burning property of a material. A lowering of the FIGRA value means a lowering of the fire growth in a material. As shown in Table 6.2, the GRE-DP/Zr has the lowest FIGRA value (4.1 kW/m²-s), followed by GRE-DP/Re (5.4 kW/m²-s) and GRE-DP/Ce (5.9 kW/m²-s), which are significantly lower than that of the control sample (7.7 kW/s). The lower FIGRA number indicates that the presence of ceramic coatings could provide an effective thermal barrier property to the composite and hence, reduce the fire risk. Although these three coatings helped in reducing the PHRR and FIGRA values of the composite, the THR increased (see Table 6.2) due to extra resin in the coating.

![Figure 6.4: Charred residues of the control, GRE-DP/Ce, GRE-DP/Re and GRE-DP/Zr samples at the end of the test at 50kW/m² with an ignition source](image)

At the end of the experiments, a thin ceramic layer was left on the surface for all the coated samples. Figure 6.4 (b) shows that the sample GRE-DP/Ce, containing low-melting silicate glass, left a thin silicate char layer which probably is due to the components of the Ceepree formulation melting (the melting temperature is ~350°C [5]) and forming a crystalline state of the silicate layer on the surface during the burning of the resin binder of the coating. GRE-DP/Re contains Al₂TiO₅, which has a very high
melting point (>1800 °C) [3]. The Recoxit powder layer remained at the end of experiment (Figure 6.4 (c)). Similarly in GRE-DP/Zr sample, which contains 3-7% yttria doped zirconia, the zirconia powder residue can be seen on the surface in Figure 6.4 (d).

6.1.4 The effect of varying heat fluxes on flammability

Effect of heat flux on the cone parameters of all samples is clearly seen in Table 6.2 and Figure 6.2. At 20 kW/m² heat flux, the control sample ignited at 118 s and has a PHRR value of 538 kW/m² at 142 s. While, the GRE-DP/Ce and GRE-DP/Zr samples had similar TTI values to the control sample, the GRE-DP/Re sample had the longest TTI of 140 s. These three coatings could decrease the PHRR and FIGRA values by up to 20 % compared to the control sample. With increasing heat flux from 20 to 50 kW/m², the value of PHRR increases, whereas TTI and time-to-PHRR decreases for all samples. This also results in an increase in the FIGRA values with increasing heat flux. This is more clear from Figure 6.5 where change in TTI, PHRR, T\textsubscript{PHRR} and FIGRA of the each coated sample w.r.t the control sample (ΔTTI = TTI of sample – TTI of control sample) as a function of heat flux are plotted. Figure 6.5 (a) shows that the ignition time of all coated samples decreased and became lower than that observed for the control sample when the heat flux increased, except for GRE-DP/Re, which show a slightly increased TTI compared to the other two coated samples. These results are consistent with the results in Section 6.1.3, which indicate that these ceramic coatings had little effect on reducing time-to-ignition of the composite. However, these three coatings could provide a better thermal barrier effect to that of the composite, represented by more than a 20% reduction in PHRR and 30% increase in time-to-PHRR values compared to the control sample. The reduction in PHRR is more pronounced at higher heat fluxes, especially, at 50 kW/m², where a significant difference between the control and GRE-DP/Re and GRE-DP/Zr samples is observed (see Figure 6.5 (b)). However, the delay in T\textsubscript{PHRR} is more pronounced at lower heat fluxes (Figure 6.5 (c)). The FIGRA values for all the coated samples are lower than the control samples at each respective heat flux (see Figure 6.5 (d)). The zirconia and Recoxit ceramic powders showed better thermal barrier performance than Ceepree at the respective heat fluxes. This is due to difference in the thermal conductivity
values and % particle deposition of these three powders in the coatings, as discussed earlier.

![Graphs showing thermal barrier effect](image)

**Figure 6.5**: \( \Delta \) parameters (change w.r.t control) for a) \( \Delta \text{T}_\text{TTI} \) b) \( \Delta \text{PHRR} \) c) \( \Delta \text{T}_\text{PHRR} \) and d) \( \Delta \text{FIGRA} \) of the coated samples as a function of heat flux for GRE-DP/Ce, GRE-DP/Re and GRE-DP/Zr

### 6.1.5 Thermal barrier effect of the ceramic particle coatings using a flame retarded epoxy binder

The thermal barrier effect of these coatings was investigated by the temperature profiles at the surface (\( T_s \)) and at the back surface (\( T_b \)) of the laminates, which were recorded during the cone experiments at different heat fluxes (see Section 6.1.3). The results are presented in Figure 6.6 and the extracted numerical data in terms of time-to-reach the
glass transition temperature (180 °C) and the pyrolysis temperature (250 °C) are presented in Table 6.3.

Table 6.3: The time required to reach the selected temperatures at the back surface for the Control, GRE-DP/Ce, GRE-DP/Zr and GRE-DP/Re samples at different heat fluxes

<table>
<thead>
<tr>
<th>Heat flux (kW/m²)</th>
<th>Sample</th>
<th>Time (s) to reach 180 °C</th>
<th>Time (s) to reach 250 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Surface</td>
<td>Back surface</td>
</tr>
<tr>
<td>20</td>
<td>Control</td>
<td>39 ±1</td>
<td>62 ±6</td>
</tr>
<tr>
<td></td>
<td>GRE-DP/Ce</td>
<td>24 ±1</td>
<td>105 ±8</td>
</tr>
<tr>
<td></td>
<td>GRE-DP/Re</td>
<td>33 ±1</td>
<td>109 ±6</td>
</tr>
<tr>
<td></td>
<td>GRE-DP/Zr</td>
<td>26 ±2</td>
<td>106 ±5</td>
</tr>
<tr>
<td>30</td>
<td>Control</td>
<td>24 ±1</td>
<td>56 ±2</td>
</tr>
<tr>
<td></td>
<td>GRE-DP/Re</td>
<td>25 ±2</td>
<td>75 ±4</td>
</tr>
<tr>
<td></td>
<td>GRE-DP/Zr</td>
<td>26 ±1</td>
<td>78 ±11</td>
</tr>
<tr>
<td>40</td>
<td>Control</td>
<td>19 ±1</td>
<td>46 ±4</td>
</tr>
<tr>
<td></td>
<td>GRE-DP/Ce</td>
<td>21 ±1</td>
<td>55 ±6</td>
</tr>
<tr>
<td>50</td>
<td>Control</td>
<td>17 ±1</td>
<td>43 ±2</td>
</tr>
<tr>
<td></td>
<td>GRE-DP/Zr</td>
<td>15 ±1</td>
<td>57 ±6</td>
</tr>
</tbody>
</table>

Note: [+ ] indicates an increase in ∆T with respect to the control.
Figure 6.6: The back surface temperature ($T_B$) as a function of time for the control, GRE-DP/Zr, GRE-DP/Ce and GRE-DP/Re samples at (a) 20, (b) 30, (c) 40 and (d) 50 kW/m$^2$ heat fluxes

The thermal barrier effects of these coating can be seen from Figure 6.6 (a-d), which shows that GRE-DP/Ce, GRE-DP/Re and GRE-DP/Zr coated samples generated a slower temperature rise at the back surface (un-exposed) compared to the control laminate at respective heat fluxes. With increasing the heat flux from 20 to 50 kW/m$^2$, for each sample the temperature rise rate at the back surface increased. At 20 and 30 kW/m$^2$, a significant difference in temperatures at different times between control and three coated samples can be observed. GRE-DP/Re and GRE-DP/Zr samples showed slower temperature increase rate than sample GRE-DP/Ce (see Figure 6.6 (a) and (b)). However, at heat fluxes higher than 30 kW/m$^2$, the difference in temperature rise at back surface between uncoated and coated samples is less, and also all the coated samples observed similar trend of temperature rise, except at 50 kW/m$^2$ heat flux (Figure 6.2 (d)), where the GRE-DP/Zr sample showed different results. It has the slowest temperature rise at back surface compared to the other samples. The slower rise in temperature at these heat fluxes
can be clearly seen by the increase in time to reach their selected temperatures (Table 6.3). For example, at 20 kW/m², in GRE-DP/Ce, GRE-DP/Zr and GRE-DP/Re samples, the coatings increased the time to reach 180 °C at back surface by 43, 47 and 44 s compared to the control sample. Moreover, the coatings could delay the time to reach 250 °C by more than 50 s compared to control sample (see in Table 6.3). With increasing heat flux from 20 to 50 kW/m², the time to reach both temperature points (180 and 250 °C) decreased. GRE-DP/Zr and GRE-DP/Re samples showed better thermal barrier performance than GRE-DP/Ce. These observations are consistent with the cone results in Section 6.1.3, which show that GRE-DP/Re and GRE-DP/Zr samples have lower PHRR and FIGRA values than GRE-DP/Ce. Hence, zirconia and Reoxit have higher thermal barrier efficiency to prevent the heat penetration from heat exposed surface to underlying composite laminate specimen than Ceepree.

### 6.1.6 Conclusions

From the results, it can be concluded that although 30-40 wt% of ceramic particles can be deposited on the surface of GRE composites by using 30 wt% of the resin binder, the use of the paint brush/roller techniques does not result in completely covering the surface of the GRE composite laminate with the ceramic particles. In terms of flammability, those ceramic particle coatings containing the DOPO flame retarded epoxy resin binder provided an effective insulative thermal barrier property to reduce PHRR values, decrease in FIGRA index and delay in $T_{PHRR}$ values, and, thus, an improvement of fire resistance performance of composite materials. However, the coatings reduced the TTI of the composite. The decrease in TTI was due to the flammable resin-rich surface. These three ceramic coatings could also significantly retard the mass loss rate compared to the control sample. In terms of thermal barrier properties, at low heat fluxes all the ceramic coatings provided effective thermal barrier/insulative char layers, which helped to delay the heat penetration from surface to underlying layers, measured as a slower rise in temperature and an increased time to reach the glass transition temperature (180 °C) and the pyrolysis temperature (250 °C) at the back surface of the laminate. The best results were shown by the Reoxit and zirconia ceramic particle coatings.
It is noteworthy that these ceramic coatings could provide a better thermal barrier performance if the ceramic particles completely covered the surface. Also, some flame retardant chemicals should also be present in the surface coating layer in order to delay/stop ignition of the resin binder, as these ceramic powders act only as thermal insulators, not flame retardants.

6.2 Part II: Flammability behaviour of the resin to be used as binder in coatings

Based on the results from Part I, the aim of this part was to select a suitable resin binder, which has inherent flame retardant properties and can prolong the TTI of these ceramic coatings. The flame retarded resin will be used to coat the composites in a similar manner as for the ceramic coatings. The resins used were an epoxy resin modified with various additives, i.e. ammonium polyphosphate (APP); tris (tribromoneopentyl) phosphate (FR372); pentaerythritol phosphate (NH1197); and a resole phenolic resin (Phe, DUREZ33156). Details are given in Section 3.4.2.2, Chapter 3. Resin-coated samples were tested for flammability using a cone calorimeter in the horizontal mode at 25 kW/m² with an ignition source (for details see Section 3.7.1 in Chapter 3). The exact thickness and mass of each resin binder coating on the surface of the GRE laminates are given in Table 6.4.

Table 6.4: Physical properties of the flame retarded epoxy resins and phenolic resin coatings applied on the GRE laminates sized 75 x 75 mm

<table>
<thead>
<tr>
<th>Sample</th>
<th>Resin content in laminate (wt%)</th>
<th>% FR in coatings (wt%)</th>
<th>Mass of coating (g)</th>
<th>Coating thickness (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>38 ±2</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>GRE-EP/APP</td>
<td>39 ±3</td>
<td>20</td>
<td>0.52 ±0.02</td>
<td>115 ±15</td>
</tr>
<tr>
<td>GRE-EP/NH1197</td>
<td>41 ±2</td>
<td>20</td>
<td>0.53 ±0.01</td>
<td>320 ±1</td>
</tr>
<tr>
<td>GRE-EP/FR372</td>
<td>39 ±2</td>
<td>20</td>
<td>0.51 ±0.01</td>
<td>115 ±5</td>
</tr>
<tr>
<td>GRE-Phe</td>
<td>40 ±1</td>
<td>-</td>
<td>0.44 ±0.03</td>
<td>115 ±5</td>
</tr>
</tbody>
</table>

Note: GRE-Phe sample was coated by neat phenolic resin without any flame retardant.
6.2.1 Flammability behaviour of the GRE composites with different binder coatings

The HRR curves as a function of exposure time of the control and binder coated GRE composite samples at 25 kW/m$^2$ heat flux are shown in Figure 6.7 and all derived results are presented in Table 6.5.

![Figure 6.7: (a) HRR versus time and (b) mass loss versus time curves for the control and binder coated GRE composite samples at 25 kW/m$^2$ with an ignition source](image)

<table>
<thead>
<tr>
<th>Sample</th>
<th>TTI (s)</th>
<th>Flame out time (s)</th>
<th>PHRR (kW/m$^2$)</th>
<th>TPHRR (s)</th>
<th>THR (MJ/m$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>119 ±1</td>
<td>214 ± 7</td>
<td>838 ± 8</td>
<td>161 ±3</td>
<td>39.1 ±2.6</td>
</tr>
</tbody>
</table>

Note: The value in brackets, [ ], represent the increase (+) or reduction (−) in a given fire reaction parameter for the resin coated GRE laminates relative to the control sample.
In this section, the flammability properties of the GRE composites coated with different resin formations are discussed only in terms of TTI, PHRR and THR. As can be seen from Figure 6.7, (a) the resin coated samples showed a single peak HRR-curves, similar to that of the control sample, but of less intensity representing lower heat release rate. All flame retarded epoxy resin coated samples (GRE-EP/APP, GRE-EP/NH1193 and GRE-EP/FR372) have relatively earlier ignition compared to the control sample as seen in Table 6.5. This is due to the fact that the phosphorus compounds APP, NH1179 and FR372 flame retardants start to decompose at lower temperatures than the resin [1,6]. On the other hand, the application of the phenolic resin as surface coating delayed TTI value from 119 s in the control to 127 s in GRE-Phe. This probably is due to the decomposition reaction of phenolic resin occurring over a temperature range of 400-500 °C [7,8], whereas epoxy resin starts to decomposing at 350 °C [6,9]. These observations are consistent with the mass loss results in Figure 6.7 (b), showing that the % mass loss of GRE-Phe is lower than that of all the other flame retarded, epoxy-coated samples. The sample GRE-EP/APP shows the longest flame-out time of 283 s, the PHRR had decreased from 838 kW/m² for the control sample to 577 kW/m² whilst the T_{PHRR} increased by 10 s compared to that of the control sample. The GRE-EP/NH1197 and GRE-Phe sample showed a similar behaviour to the GRE-EP/APP, with slightly higher PHRR values (637 kW/m² at 152 s for GRE-EP/NH1197 and 750 kW/m² at 168 s for GRE-Phe) and shorter flame out times, the values being lower than that of the control sample. The GRE-EP/FR372 sample did not show any improvement in terms of increasing TTI and reducing PHRR, when compared with GRE-EP/APP, GRE-EP/NH1197 and GRE-Phe. All of the flame retarded epoxy resins, except GRE-EP/APP, slightly increased their THR values compared to that of the control sample. Thus, these coatings prolonged the burning time of the GRE composite. GRE-Phe was also not successful in reducing PHRR, but delayed T_{PHRR} by 7 s.

6.2.2 Conclusions

From the results in this part, it can be concluded that APP is the most effective flame retardant to improve the flammability of the epoxy resin, followed by NH1197 and FR372. However, the presence of flame retardants, such as APP and NH1197 in epoxy
resin surface coatings did not improve the time-to-ignition of the GRE composite, which is an important parameter for a thermal barrier coating. On the other hand, the phenolic resin surface coating provided the prolonged time-to-ignition and lower flammability to GRE composite, e.g. 10% reduction in PHRR values of GRE-Phe compared to the uncoated control sample. Based on this study, the phenolic resin has been chosen to be used as a suitable binder for the next set of ceramic particle coating experiments.

6.3 Part III: Ceramic particle coatings using a phenolic resin

In this part, five different types of ceramic particles were used with the phenolic resin binder to prepare coatings for the GRE composite. The ceramic particles included nanoclay, nanosilica, Flekashield, Recoxit and zirconia. An additional coating, Flekashield and zirconia in a 1:2 ratio were also used. The coatings were applied on the GRE composite surfaces using a K-bar coater instead of a paint brush and roller as in the previous coatings (Part I). Two sets of samples were prepared, and the first set was prepared as mentioned above (Table 6.6 (a)). In the second set (Table 6.6 (b)), additional ceramic particles were sieved using a mesh on to the wet coating, prior to the curing of that coating. The details are discussed in Section 3.4.2.3, Chapter 3. The flammability and thermal barrier properties of these coated composites were investigated using a cone calorimeter at 35 and 50 kW/m² without using the electric sparking ignition. The effects of these ceramic coatings on physical and mechanical properties of the composite laminates have been also studied. Additionally, the effect of heat on mechanical property retention after exposure to radiative heat (cone calorimeter) has also been studied by the three point blending test.

6.3.1 Physical properties of the coatings

Since each laminate was individually coated, there was variation in mass and thickness of each coating on each GRE composite as shown in Table 6.6. The ceramic particle deposition (wt%) of each coated sample was calculated as discussed in Section 3.4.2.3 (Chapter 3), and values are given in this table.
Table 6.6: Physical properties of the ceramic particle coatings using a phenolic resin binder applied on a 150 mm x 75 mm plaque of the GRE laminates

(a) Set I samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ceramic:Resin ratio in coating</th>
<th>Ceramic particle and size</th>
<th>Coating thickness (µm)</th>
<th>Mass of coating (g)</th>
<th>Ceramic particle deposited (wt%, w.r.t laminate)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GRE-P/30B</td>
<td>25:75</td>
<td>Nanoclay (&lt; 10 µm)</td>
<td>143 ±9</td>
<td>2.04 ±0.11</td>
<td>1.18±0.05</td>
</tr>
<tr>
<td>GRE-P/Si</td>
<td>10:90</td>
<td>Nanosilica (&lt; 12 nm)</td>
<td>125 ±8</td>
<td>0.94 ±0.14</td>
<td>0.23±0.04</td>
</tr>
<tr>
<td>GRE-P/Flek</td>
<td>20:80</td>
<td>Flekashield (300-400 µm)</td>
<td>290 ±19</td>
<td>2.99 ±0.52</td>
<td>1.46±0.19</td>
</tr>
<tr>
<td>GRE-P/Re</td>
<td>70:30</td>
<td>Recoxit (&lt; 40 µm)</td>
<td>345 ±30</td>
<td>5.83 ±0.82</td>
<td>9.67±1.01</td>
</tr>
<tr>
<td>GRE-P/Zr</td>
<td>70:30</td>
<td>Zirconia (&lt; 60 µm)</td>
<td>469±48</td>
<td>8.20±0.33</td>
<td>14.09±0.81</td>
</tr>
</tbody>
</table>

(b) Set II samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ceramic:Resin ratio in coating</th>
<th>Ceramic particle and size</th>
<th>Coating thickness (µm)</th>
<th>Mass of coating (g)</th>
<th>Ceramic particle deposited (wt%, w.r.t laminate)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GRE-P/FlekS</td>
<td>20:80</td>
<td>Flekashield (300-400 µm)</td>
<td>297 ±49</td>
<td>3.67 ±0.21</td>
<td>1.75±0.15</td>
</tr>
<tr>
<td>GRE-P/ReS</td>
<td>70:30</td>
<td>Recoxit (&lt; 40 µm)</td>
<td>645 ±28</td>
<td>7.97 ±0.73</td>
<td>15.86±1.17</td>
</tr>
<tr>
<td>GRE-P/ZrS</td>
<td>70:30</td>
<td>Zirconia (&lt; 60 µm)</td>
<td>485 ±39</td>
<td>9.00 ±0.42</td>
<td>18.37±1.58</td>
</tr>
<tr>
<td>GRE-P/FZrS</td>
<td>30 (1:2):70</td>
<td>Flekashield and Zirconia</td>
<td>398 ±44</td>
<td>3.97 ±0.43</td>
<td>2.94±0.82</td>
</tr>
</tbody>
</table>

Note: *Mass of GRE laminate (150 mm x 75 mm) ~ 41 g

The results in Table 6.6 (a) show that with 10 wt% of nanosilica in the coating, a 125 µm thick coating in GRE-P/Si was obtained, with 0.23 wt% particle deposition on the laminates. The use of 25 wt% of Cloisite 30B in GRE-P/30B yielded a 143 µm coating thickness with 1.18 wt% particle deposition, and 20 wt% of Flekashield (GRE-P/Flek) gave a 290 µm coating thickness with 1.46 wt% particle deposition. In the cases of Recoxit and zirconia, 70 wt% of ceramic particles in the coating gave 345 µm thickness with 9.67 wt% and 469 µm thickness with 14.09 wt% particle deposition of GRE-P/Re
and GRE-P/Zr, respectively. Where additional ceramic particles were applied by dry sieving onto the coated surface (i.e. following application of the ceramic-phenolic coating suspension), the particle deposition (wt%) increased from 1.46 to 1.75 % in GRE-P/FlekS, from 9.67 % to 15.86 % in GRE-P/ReS and from 14.09 % to 18.37 % in GRE-P/ZrS samples (see Table 6.6 (a and b)). The thickness of these coatings also increased. For the combination of Flekashield (10 wt%) and zirconia(20 wt%) in GRE-P/FZrS sample 398 µm thick coating with 2.94 wt% particle deposition could be obtained.

6.3.2 Surface characterisation

SEM images of the surfaces of the ceramic particle-coated GRE composite samples are shown in Figure 6.8. The results show that the distribution of particles on the surface is uniform indicating a good dispersion of the particles without large agglomerations in the resin of the coatings. However, it can be also seen that at some places the particles do not completely cover the surface (see Figure 6.8). As can be seen from image (a), the surface of nanoclay 30B coated sample is relatively smoother than all the other samples. In all the coated samples particles can be clearly seen on the surface. In the case of GRE-P/Si, the coating is uniform although micro-fractures are clearly visible on the surface, which is probably due to the solvent evaporation during curing of the coating, which induces in-plane tensile stresses that can cause the fractures of the coating [10, 11]. This is commonly observed for colloidal dispersion coating systems [12]. Consequently, the surface morphology of the samples with additional ceramic particles (GRE-P/FlekS, GRE-P/ReS and GRE-P/ZrS) is rougher, the roughness of which varies as a function of the concentration of additional ceramic particles on the surface as clearly seen at high magnification (50 µm scale), see Figure 6.8 (e, g and i). The additional particles of Recoxit and zirconia on the coated surface help in significantly increasing the concentration of ceramic particles on the surface and also improve surface coverage. The Flekashield particle coating, however, is not very uniform (Figure 6.8 (e)), which is likely due to the larger particle size of Flekashield compared to zirconia and Recoxit (Table 6.6).
Figure 6.8: SEM images of all coated sample surfaces at various magnifications
6.3.3 Flammability behaviour of GRE composites with ceramic particle coatings using a phenolic binder

The flammability behaviour of GRE composite laminates with/without ceramic particle coatings using the phenolic resin binder was evaluated by the cone calorimeter at 35 and 50 kW/m² without using an ignition source. An ignition source was not used to avoid early ignition of the resin used as a binder in the ceramic particle coatings as already discussed in Section 3.7.1 (Chapter 3).

6.3.3.1 Flammability at 35 kW/m² heat flux in the absence of ignition source

The HRR vs. time curves of control and all each coated samples are shown in Figure 6.9 while the extracted numerical data for all samples are presented in Table 6.7. Also, the % mass loss versus time curves of the control and all coated samples are shown in Figure 6.10.

Table 6.7: Cone calorimetric data for control and all coated samples at 35 kW/m² heat flux without an ignition source

(a) Set I samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Specimen No.</th>
<th>% Particle deposition</th>
<th>TTI (s)</th>
<th>PHRR (kW/m²)</th>
<th>TPHRR (s)</th>
<th>THR (MJ/m²)</th>
<th>FIGRA (kW/m²-s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>1,2,3</td>
<td>-</td>
<td>104±10</td>
<td>526±26</td>
<td>136±16</td>
<td>36.8±6.6</td>
<td>3.8±0.6</td>
</tr>
<tr>
<td>GRE-Phe</td>
<td>1,2,3</td>
<td>-</td>
<td>108±12</td>
<td>490±12</td>
<td>165±20</td>
<td>46.4±3.8</td>
<td>3.0±0.5</td>
</tr>
<tr>
<td>GRE-P/30B</td>
<td>1,2</td>
<td>1.14±0.10</td>
<td>135±2</td>
<td>448±49</td>
<td>177±19</td>
<td>44.5±1.7</td>
<td>2.5±0.1</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>1.17</td>
<td>153</td>
<td>410</td>
<td>202</td>
<td>35.1</td>
<td>2.0</td>
</tr>
<tr>
<td>GRE-P/Si</td>
<td>1,3</td>
<td>0.19±0.30</td>
<td>185±62</td>
<td>420±3</td>
<td>228±76</td>
<td>44.4±2.0</td>
<td>2.1±0.7</td>
</tr>
<tr>
<td></td>
<td>2*</td>
<td>0.28</td>
<td>-</td>
<td>4</td>
<td>16</td>
<td>0.00</td>
<td>0.0</td>
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<tr>
<td>GRE-P/Flek</td>
<td>1,2</td>
<td>1.41±0.20</td>
<td>201±9</td>
<td>385±39</td>
<td>233±1</td>
<td>29.1±3.1</td>
<td>1.6±0.2</td>
</tr>
<tr>
<td></td>
<td>3*</td>
<td>1.44</td>
<td>-</td>
<td>40</td>
<td>448</td>
<td>7.2</td>
<td>0.1</td>
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<tr>
<td>GRE-P/Re</td>
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<td>8.47</td>
<td>124</td>
<td>400</td>
<td>152</td>
<td>33.5</td>
<td>2.6</td>
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<tr>
<td></td>
<td>2,3</td>
<td>8.92±0.01</td>
<td>145±7</td>
<td>456±29</td>
<td>195±5</td>
<td>39.7±1.8</td>
<td>2.3±0.2</td>
</tr>
<tr>
<td>GRE-P/Zr</td>
<td>1</td>
<td>14.07</td>
<td>105</td>
<td>459</td>
<td>160</td>
<td>43.9</td>
<td>2.9</td>
</tr>
<tr>
<td></td>
<td>2,3</td>
<td>14.83±0.01</td>
<td>126±1</td>
<td>429±1</td>
<td>180±1</td>
<td>44.4±2.1</td>
<td>2.4±0.1</td>
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</tbody>
</table>
### (b) Set II samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Specimen No.</th>
<th>% Particle deposition</th>
<th>TTI (s)</th>
<th>PHRR (kW/m²)</th>
<th>T_PHRR (s)</th>
<th>THR (MJ/m²)</th>
<th>FIGRA (kW/m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GRE-P/FleKS</td>
<td>1,2*</td>
<td>4.30 ±0.50</td>
<td>-</td>
<td>35 ±62</td>
<td>363 ±77</td>
<td>6.6 ± 6.5</td>
<td>0.12 ±0.1</td>
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<td>3</td>
<td>4.22</td>
<td>282</td>
<td>222</td>
<td>328</td>
<td>29.6</td>
<td>0.7</td>
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<tr>
<td>GRE-P/ReS</td>
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<td>15.84</td>
<td>144</td>
<td>482</td>
<td>178</td>
<td>30.4</td>
<td>2.7</td>
</tr>
<tr>
<td></td>
<td>2,3</td>
<td>16.32 ±0.01</td>
<td>157 ±5</td>
<td>443 ±10</td>
<td>227 ±3</td>
<td>36.4 ±1.1</td>
<td>1.9 ±0.1</td>
</tr>
<tr>
<td>GRE-P/ZrS</td>
<td>1,2</td>
<td>17.25 ±0.70</td>
<td>139 ±15</td>
<td>470 ±8</td>
<td>193 ±11</td>
<td>44.1 ±1.5</td>
<td>2.4 ±0.2</td>
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<tr>
<td></td>
<td>3</td>
<td>17.93</td>
<td>172</td>
<td>325</td>
<td>212</td>
<td>26.3</td>
<td>1.5</td>
</tr>
<tr>
<td>GRE-P/FZrS</td>
<td>1,2</td>
<td>3.29 ±0.30</td>
<td>141 ±3</td>
<td>483 ±25</td>
<td>178 ±3</td>
<td>45.7 ±2.1</td>
<td>2.7 ±0.1</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>3.37</td>
<td>268</td>
<td>347</td>
<td>312</td>
<td>35.6</td>
<td>1.1</td>
</tr>
</tbody>
</table>

Note: * indicates that the sample did not ignite; FIGRA is fire growth rate index, defined as the ratio of PHRR and the time at which PHRR occurs.

---

(a) Control
- **GRE-Phe**

(b) Control
- GRE-P/30B 1
- GRE-P/30B 2
- GRE-P/30B 3

(c) Control
- GRE-P/Si 1
- GRE-P/Si 2*
- GRE-P/Si 3
Figure 6.9: HRR versus time curves of the control and coated samples at 35 kW/m² heat flux without an ignition source [* indicates that the sample did not ignite]
Figure 6.10: Mass loss versus time curves of the control and coated samples at 35 kW/m² heat flux without an ignition source.

Figure 6.11: Digital images of charred residues of all samples after exposure to 35 kW/m² heat flux without an ignition source.
The results show that at 35 kW/m² the control GRE sample ignited after 104 s of continued exposure to the heat without an ignition source. Figure 6.9 (a) shows a sharp and intense single peak of HRR of 526 kW/m² at 136 s. The process of heat release of the control sample finished within 300 s (see Table 6.7 (a)). With neat phenolic resin coating (without any nano/micro particles) on GRE composite, GRE-Phe shows a single peak HRR-curves as seen for the control sample, with similar intensity but slightly broader peak representing the longer burning, resulting in higher total heat release (THR) due to additional phenolic resin on GRE laminate surface. With respect to the control sample, the time-to-ignition (TTI) of GRE-Phe has not increased much, but time-to-PHRR (T_PHRR) is delayed by 30 s, PHRR decreased from 526 to 490 kW/m² and FIGRA decreased by 20%. As can be seen from Figure 6.10 (b), the resin matrix in GRE-Phe sample is totally burnt out. However, there is more carbonaceous char residue left on the surface of glass fibres compared to that in control sample. These observations indicate that while the inherently flame retardant character of the phenolic resin reduces PHRR and increases T_PHRR. However, it had little effect on TTI, which is contradictory to the results presented in Part II (Section 6.2.1). It should be noted that in the Part II study the flammability of different resin binders was studied at 25 kW/m² in the presence of an ignition source, whereas here no ignition source was used. Hence, the results are different.

As clearly seen in Figure 6.9 (b-j), the HRR curves of the samples coated with nanoclay, nanosilica, Flekashield, Recoxit and zirconia coatings are significantly different from that of the control sample, with delayed TTI, a less intense peak and broader HRR curves representing a longer time-to-ignition, lower combustible volatiles production and lower heat release rates. However, slight variations in HRR curve results of each specimen of a ceramic particle coated sample were observed, which is due to different concentrations of the particles on each sample and in some cases the ceramic particles are not fully covering the surface to provide an effective barrier layer for a period of time.

For the 30B nanoclay coating, two specimens of GRE-P/30B with 1.14 wt% particle deposition ignited at 133 s, the PHRR is reduced by 15 % and T_PHRR is delayed by 31 s compared to the control sample as can be seen in Table 6.7 (a). With higher particle deposition, in GRE-P/30B-3 sample, the TTI is further increased to 153s, PHRR decreased to 410 kW/m² and T_PHRR increased to 202 s. The reduction in PHRR and increase in T_PHRR in all GRE-P/30B samples also results in a significant reduction in the fire growth index.
(FIGRA) values. The nanoclay coating reduced the FIGRA values of the uncoated laminate from 3.8 to 2.0 kW/m²·s. However, the THR values of GRE-P/30B samples are higher than the control sample due to HRR curves for those GRE-P/30B samples being broader than that of the control sample (Figure 6.9 (b)), indicating a prolonged burning time. This is commonly observed for coatings providing passive fire protection [13,14]. These results suggest that ~ 143 μm thick nanoclay (Cloisite 30B)/phenolic resin coating (sample GRE-P/30B) was effective in increasing TTI, and $T_{PHRR}$ and reducing PHRR compared to the uncoated GRE composite, which is due to the combined effect of the nanoclay particles and inherently flame retardant phenolic binder. The phenolic resin helps in maintaining a higher TTI, whereas the silicate layer on the surface acts as a barrier to degradation of the resin binder of the coating, thus providing a thermal barrier protection to the underlying structure in order to inhibit heat and mass transfer to the pyrolysis zone. This then slows down the combustion process of the GRE composite [15]. As can be clearly seen at the end of the test, a thin layer of silicate residue was left on the surface of the laminate, but this being very thin and flimsy, is not capable of retaining the integrity of the laminate for a long time (Figure 6.11 (c)).

The use of nanosilica particles showed better cone results than those for nanoclay coated samples as can be seen from Figure 6.9 (c) and Table 6.7 (a). With 0.28 % deposition, the GRE-P/Si-2 sample did not ignite. However, the samples with lower particle depositions (GRE-P/Si-1 and GRE-P/Si-3) ignited. With respect to the control sample, the TTI and $T_{PHRR}$ of GRE-P/Si have significantly increased by ~ 80 s and ~100 s, respectively, while the PHRR decreased from 526 to 420 kW/m² and FIGRA decreased by 45 %. The THR value of GRE-P/Si samples, however, was increased to the same extent as in the case of GRE-P/30B, when compared to the control sample. This observation indicates that even though the nanosilica coating has a lower particle concentration than the nanoclay coating, it provides a better thermal barrier effect in terms of delay in the TTI and reduction in PHRR, FIGRA values. This is due to the fact that particle size of nanosilica is smaller than that of the 30B nanoclay (see Table 6.6 (a)) and also the structure of nanosilica does not have the narrow gallery structure of the silicate layer as in the 30B nanoclay [16,17], which may cause in a better structure of the silicate layer formation of nanosilica coating than the nanoclay coating. However, a very thin charred layer of GRE-P/Si was observed similar to that in the case of GRE-P/30B at the end of the test (see Figure 6.11 (d))
The cone results for the sample GRE-P/Flek in Figure 6.9 (d) and Table 6.7 (a) show better fire retardant improvements than those observed for the GRE-P/30B and GRE-P/Si samples. One sample with 1.44 wt% particle deposition (GRE-P/Flek-3) did not ignite. Although the other two specimens with lower particle deposition (GRE-P/Flek-1 and GRE-P/Flek-2) ignited and the TTI was considerably increased, i.e. to 201 s, PHRR decreased to 385 kW/m² and \( T_{\text{PHRR}} \) increased to 233 s from respective values 104 s, 526 kW/m² and 136 s of the control sample. The THR and FIGRA values for GRE-P/Flek are also very low (29.1 MJ/m² and 1.6 kW/m²-s) compared to the rest of the samples, which shows the higher thermal barrier efficiency of the Flekashield coating than the other coatings as clearly seen from Table 6.6 (a). This is because the Flekashield particles (containing small platelets of E-glass and particles of low-melting silicate glass) can be melted and form a hard structure of an aligned glass platelets layer to protect the underlying composite from heat/fire during the burning of the resin binder. The hard glassy layer acts as a physical insulating barrier reduction of the heat transfer and mass transport of combustible volatiles and/or oxygen, protecting the underlying laminate structure. A very thin glassy silicate layer was left on the laminate surface at the end of the cone experiment (see Figure 6.11 (e)), which is similar to that observed for GRE-P/30B and GRE-P/Si. The layer laying was very thin, and loss of structural integrity of the GRE laminate (delamination) was also observed.

The application of Recoxit and zirconia coatings showed least effect on improvement in fire retardant properties. The cone results for the samples GRE-P/Re and GRE-P/Zr are not as good as those for other coated samples as can be seen from Table 6.6 (a) and Figure 6.9 (e and f). With 8.92 wt% of Recoxit and 14.83 wt% of zirconia depositions, the TTI and \( T_{\text{PHRR}} \) are increased, while the PHRR is reduced, but not to the same extent as in the other ceramic-coated samples. This is probably due to the Recoxit and zirconia particles having very high melting points and so could not form a hard thermal barrier ceramic layer similar to that of the nanosilica and Flekashield coatings. The thermal barrier performance of Recoxit and zirconia particles is due to their low thermal conductivity. They mainly act by physical means to diffuse heat transfer and all the volatiles generated during combustion of the resin. This can be supported by Recoxit and zirconia particles layer observed at the end of experiment (see Figure 6.11 (g and i)).
The results in Table 6.7 (b) clearly show that when additional ceramic particles are deposited on the surface in the cases of Flekashield, Recoxit and zirconia coatings, there is a considerable improvement in the delay in TTI compared to normal coatings. For instance, GRE-P/Flek, GRE-P/Re and GRE-P/Zr ignited at 201, 145 and 126 s, while, GRE-P/FlekS, GRE-P/ReS and GRE-P/ZrS samples ignited at 282, 157 and 172 s, respectively. Other parameters, i.e. PHRR, FIGRA, THR, in GRE-FlekS, GRE-ReS and GRE-P/ZrS samples were also further affected when compared to each coated sample without the extra ceramic particles. This suggests that the additional ceramic particles help in completely covering the surface, resulting in significantly increased TTI, and further reduced PHRR, FIGRA and THR values. On comparing the samples where a combination of Flekashield and zirconia particles were used in the coating (GRE-P/FZrS), the results in Table 6.6 (b) and Figure 6.9 (i) clearly show that the TTI and $T_{\text{PHRR}}$ values of GRE-P/FZrS are considerable longer than that of GRE-P/ZrS. Here Flekashield melts and spreads on the surface, specifying its glassy layer plus zirconia (see Figure 6.10 (k)). This helps in improving the time-to-ignition of the zirconia coatings. However, there is little effect on other parameters, i.e. PHRR, FIGRA values.

The mass loss curves during the cone experiments, see Figure 6.10, also show the thermal barrier effect of all the ceramic particle coatings. As clearly seen in Figure 6.10 (a), there is no difference in the mass loss rate between the control and GRE-Phe samples, whereas all ceramic-coated samples significantly retarded the mass loss rate when compared to the control sample, especially for the GRE-P/Flek and GRE-P/FlekS samples (Figure 6.10 (a-d)). The effect of additional particles on the thermal barrier efficiency of all the ceramic-coated samples show a further reduction in mass loss rate when compared to their normal coated samples. This observation is consistent with the cone results in the above discussions.

The effects of particle and coating thicknesses on various parameters are clearly shown in Figure 6.12, where the $\Delta$ parameters (TTI, PHRR, $T_{\text{PHRR}}$ and FIGRA) of the each coated sample w.r.t the control sample as a function of coating thickness are plotted.
Figure 6.12: \( \Delta \) parameters a) TTI b) PHRR c) \( T_{\text{PHRR}} \) and d) FIGRA of the each coated sample w.r.t control sample as a function of coating thickness at 35 kW/m\(^2\) without an ignition source [* indicates that the sample did not ignite]
Figure 6.12 (a-d) shows that with additional particles, the Flekashield, Recoxit and zirconia coatings generated on improvement in all the terms (TTI, PHRR, TPHRR and FIGRA) when compared to each respective coating without the extra particles, especially for the ~ 400 µm thickness of GRE-P/FlekS which shows the best thermal barrier performance in all the terms of fire retardant improvement. Moreover, Flekashield particles in GRE-P/FZRS significantly improved the TTI and TPHRR of GRE-P/ZrS, whereas the thicker coatings of Recoxit and zirconia coatings show the least improvement in fire retardant parameters when compared to thinner coatings of nanoclay, nanosilica and Flekashield.

From the cone results at 35 kW/m² of these ceramic coatings, it can be concluded that the GRE laminates which were surface-coated by different ceramic particles containing the phenolic binder gave variable results, depending mainly upon the nature of each different ceramic particle and the particle concentration on the substrate and whether the particles completely covered the surface or some of the resin was exposed. If the surface is completely covered by ceramic particles, it is expected that the coating will provide an effective thermal barrier protection to the GRE composite. This is indicated by a significant delay in TTI or time-to-PHRR and even non-ignition of the sample. If, however, some resin binder is exposed on the surface, the underlying composite will ignite earlier and the barrier effect of the ceramic particle coating will be less.

6.3.3.2 Flammability at 50 kW/m² heat flux in the absence of an ignition source

All samples in Table 6.6, i.e. the control, GRE-Phe, GRE-P/Si, GRE-P/30B, GRE-P/FlekS, GRE-P/ReS, GRE-P/ZrS and GRE-P/FZrS, were tested using a cone calorimeter at 50kW/m² without an ignition source. The HRR vs. time curves of these samples are shown in Figure 6.13 while the extracted numerical data for all samples are presented in Table 6.8.
Figure 6.13: HRR versus time curves of the control and coated samples at 50 kW/m² heat flux without an ignition source
Table 6.8: Cone calorimetric data for the control and all coated samples at 50 kW/m$^2$ heat flux without an ignition source

(a) Set I samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Specimen No.</th>
<th>% Particle deposition</th>
<th>TTI (s)</th>
<th>PHRR (kW/m$^2$)</th>
<th>$T_{\text{PHRR}}$ (s)</th>
<th>THR (MJ/m$^2$)</th>
<th>FIGRA (kW/m$^2$-s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>1,2,3</td>
<td>-</td>
<td>48 ±2</td>
<td>691 ±11</td>
<td>68 ±6</td>
<td>38.4 ±1.6</td>
<td>9.1 ±1.2</td>
</tr>
<tr>
<td>GRE-Phe</td>
<td>1,2,3</td>
<td>-</td>
<td>54 ±0</td>
<td>659 ±2</td>
<td>76 ±12</td>
<td>43.9 ±3.1</td>
<td>8.9 ±1.4</td>
</tr>
<tr>
<td>GRE-P/30B</td>
<td>1,2,3</td>
<td>1.19 ±0.03</td>
<td>63 ±5</td>
<td>509 ±22</td>
<td>97 ±25</td>
<td>48.3 ±2.0</td>
<td>5.6 ±1.3</td>
</tr>
<tr>
<td>GRE-P/Si</td>
<td>1,2</td>
<td>0.24 ±0.02</td>
<td>67 ±1</td>
<td>528 ±12</td>
<td>96 ±4</td>
<td>36.8 ±1.8</td>
<td>5.5 ±0.1</td>
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<td></td>
<td>3</td>
<td>0.28</td>
<td>91</td>
<td>522</td>
<td>110</td>
<td>38.7</td>
<td>4.7</td>
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</table>

(b) Set II samples

<table>
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<th>Sample</th>
<th>Specimen No.</th>
<th>% Particle deposition</th>
<th>TTI (s)</th>
<th>PHRR (kW/m$^2$)</th>
<th>$T_{\text{PHRR}}$ (s)</th>
<th>THR (MJ/m$^2$)</th>
<th>FIGRA (kW/m$^2$-s)</th>
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</thead>
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<tr>
<td>GRE-P/FlekS</td>
<td>1,3</td>
<td>3.99 ±0.00</td>
<td>75</td>
<td>613</td>
<td>126</td>
<td>46.7</td>
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<tr>
<td></td>
<td>2,3</td>
<td>4.30 ±0.00</td>
<td>117 ±10</td>
<td>542 ±7</td>
<td>144 ±11</td>
<td>38.8 ±1.2</td>
<td>3.8 ±0.0</td>
</tr>
<tr>
<td>GRE-P/ReS</td>
<td>1,2</td>
<td>16.32 ±0.00</td>
<td>64 ±2</td>
<td>567 ±19</td>
<td>136 ±8</td>
<td>46.4 ±3.7</td>
<td>4.2 ±0.1</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>17.22</td>
<td>102</td>
<td>592</td>
<td>146</td>
<td>49.4</td>
<td>4.1</td>
</tr>
<tr>
<td>GRE-P/ZrS</td>
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<td>17.93 ±0.00</td>
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<td>530</td>
<td>120</td>
<td>55.0</td>
<td>4.4</td>
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<td>2,3</td>
<td>18.40 ±0.00</td>
<td>71 ±2</td>
<td>507 ±7</td>
<td>127 ±7</td>
<td>49.9 ±0.2</td>
<td>4.0 ±0.3</td>
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<tr>
<td>GRE-P/FZrS</td>
<td>1,2,3</td>
<td>3.41 ±0.00</td>
<td>73 ±3</td>
<td>565 ±11</td>
<td>117 ±2</td>
<td>48.8 ±1.5</td>
<td>4.8 ±0.5</td>
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</tbody>
</table>

Note: FIGRA is fire growth rate index, defined as the ratio of PHRR and the time to PHRR

The sample with only phenolic resin (GRE-Phe) increased the time-to-ignition of the control sample by 6 s and reduced PHRR from 691 to 659 kW/m$^2$. The $T_{\text{PHRR}}$ value was also increased from 68 s to 76 s. The variations in the HRR curve results of each specimen of a ceramic particles coated sample were also observed as being similar to those at 35 kW/m$^2$ heat flux. GRE-Si, GRE-30B, GRE-FlekS, GRE-ReS, GRE-ZrS and GRE-FZrS samples clearly show higher TTI, lower PHRR and broader HRR-curves compared to the control sample. This can indicate an effective thermal barrier protection of each ceramic particle coating at high heat flux (Figure 6.13 (b-g)). As can be seen in Table 6.8 (a), for nanoparticles, the nanoclay coatings with 1.19 wt% particle deposition (GRE-P/30B) igniting at 63 s, while the PHRR is reduced by 24 %, $T_{\text{PHRR}}$ is delayed by 29 s and FIGRA decreased by 38 % compared to the control sample. However, THR value is increased. Similarly, for GRE-P/Si samples, the TTI and $T_{\text{PHRR}}$ are increased. The PHRR is not reduced to the same extent as in the case of GRE-P/30B, but the THR value is lower.
With additional ceramic particles (see Table 6.8 (b)), the GRE-P/FlekS with 4.30 wt% particle deposition showed the best fire retardant improvements compared to those observed for the other coated samples. With respect to the control sample, the TTI values of GRE-P/FlekS have considerably increased to 117 s, the PHRR is decreased from 691 in the control to 542 kW/m² and FIGRA decreased by 58 \% without significantly increasing the THR value. For Recoxit and zirconia coatings, the improvements in the thermal stability and fire performance of the GRE-ReS and GRE-P/ZrS samples were observed to be similar to that of the GRE-P/30B and GRE-P/Si samples as can be seen from Table 6.8 (a). In the case of sample combining Flekashield and zirconia particles in the coating (GRE-P/FZrS), the results in Table 6.8 (b) and Figure 6.13 (g) show that the presence of Flekashield particles did not help in further improving the fire performance of GRE-P/FZrS when compared to GRE-P/ZrS. This is different from the observation at 35 kW/m²² heat flux. This observation indicates that Recoxit and zirconia particle coatings provide a better thermal barrier protection to the GRE composite at higher heat fluxes, rather than at low heat fluxes. This observation can be supported by the mass loss results in Figure 6.14, which shows that GRE-P/FlekS, GRE-P/ReS and GRE-P/ZrS samples significantly retarded the mass loss rate when compared to the other samples.
Figure 6.15: $\Delta$ parameters a) TTI b) PHRR c) $T_{\text{PHRR}}$ and d) FIGRA of the each coated sample w.r.t the control sample as a function of coating thickness at 50 kW/m$^2$ without an ignition source.
The thermal barrier effectiveness of these ceramic coatings at 50 kW/m\(^2\) heat flux can be clearly seen in Figure 6.15, where the Δ parameter (TTI, PHRR, T\(_{PHRR}\) and FIGRA) of the each coated sample w.r.t control sample as a function of coating thickness are plotted. The results show that the Flekashield coating showed the best thermal barrier performance, especially in terms of delay in TTI and T\(_{PHRR}\) values compared to the rest of coated samples, whilst the other ceramic coatings showed similar improvements in the PHRR and FIGRA parameters to that observed for the Flekashield coating.

To compare the effect of coatings at the different heat fluxes, the Δ parameter (TTI, PHRR, T\(_{PHRR}\) and FIGRA) of coated samples, i.e. GRE-P/30B, GRE-P/Si, GRE-FlekS, GRE-ReS and GRE-P/ZrS, at 35 and 50 kW/m\(^2\) heat fluxes are plotted as a histogram in Figure 6.16. The results show that the TTI value of each coated sample was reduced at the higher heat flux, while the Flekashield coating showed the most delay in TTI and T\(_{PHRR}\) values at both heat fluxes (Figure 6.16 (a-b)). Moreover, all the ceramic particle coatings could provide better thermal barrier effects to the composite by further reduction in PHRR and decrease in FIGRA values at higher heat fluxes, except for GRE-P/FlekS, GRE-P/Zr and GRE-
P/FZrS samples that showed a reduction in PHRR values at 50 kW/m² (see Figure 6.16 (c-d)). These results suggest that nanoclay, nanosilica, Flekashield, Recoxit and zirconia coatings could continually provide a thermal barrier protection to GRE composite from low to high heat fluxes.

6.3.4 Thermal barrier effect of the ceramic particle coatings using a phenolic binder

During the cone experiments at 35 and 50 kW/m² heat fluxes, the thermal barrier effect of all ceramic particle coatings was also evaluated using K-type thermocouples (see Section 3.7.3, Chapter 3) to measure the surface and back surface temperatures. The temperature profiles at the back surface (T_B) of each coated sample, at both heat fluxes were recorded and are plotted graphically here in Figure 6.17. The times taken for both surface and back surfaces to reach 180 and 250 ºC are given in Table 6.9.

The thermal barrier efficiency of each coating at 35 and 50 kW/m² heat fluxes can be clearly seen from Figure 6.17. The results show that at both heat fluxes the control sample shows a rapid temperature rise at the back surface. There is no significant difference in back surface temperatures of the control and GRE-Phe sample until 120 s at 35 kW/m² and ~ 60 s at 50 kW/m², after which the temperature rise is slower in samples with the phenolic coating until ~ 180 and 240 s, respectively. In GRE-P/30B and GRE-P/Si samples, there is a slower temperature rise of the back surface compared to the control sample at each heat flux. With the Flekashield, Recoxit and zirconia coatings, a significantly delay in temperature rise at the back surface can be clearly observed at 35 kW/m² heat flux (Figure 6.17 (c and e)), especially in GRE-P/ReS, GRE-P/ZrS samples with additional particles which show the most delay in the temperature rise. This indicates that the extra particles help in increasing the thermal barrier effect of these ceramic particle coatings. For the combination of Flekashield and zirconia particles, the temperature rise at the back surface of GRE-P/FZrS sample is not as slow as in the case of GRE-P/ZrS (see Figure 6.17 (e)). At 50 kW/m² heat flux, the coatings with additional particles, i.e. GRE-P/ReS, GRE-P/ZrS also show the best performance in retarding the temperature rise at the back surface of the sample.
Figure 6.17: The back surface temperature ($T_B$) as a function of time for the control and coated samples at 35 and 50 kW/m$^2$ heat fluxes without an ignition source

[* indicates that the sample did not ignite]
Table 6.9: The time required to reach the selected temperatures at the surface and back surface of all samples at different heat fluxes

(a) Set I samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>At 35 kW/m² heat flux</th>
<th>At 50 kW/m² heat flux</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Time (s) to reach 180 °C</td>
<td>Time (s) to reach 250 °C</td>
</tr>
<tr>
<td></td>
<td>Surface</td>
<td>Back surface</td>
</tr>
<tr>
<td>Control</td>
<td>18 ± 5</td>
<td>40 ± 7</td>
</tr>
<tr>
<td>GRE-P/Flek</td>
<td>17</td>
<td>48</td>
</tr>
<tr>
<td>GRE-P/Re</td>
<td>14 ± 1</td>
<td>56 ± 2</td>
</tr>
<tr>
<td>GRE-P/Zr</td>
<td>18 ± 2</td>
<td>57 ± 10</td>
</tr>
</tbody>
</table>

(b) Set II samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>At 35 kW/m² heat flux</th>
<th>At 50 kW/m² heat flux</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Time (s) to reach 180 °C</td>
<td>Time (s) to reach 250 °C</td>
</tr>
<tr>
<td></td>
<td>Surface</td>
<td>Back surface</td>
</tr>
</tbody>
</table>

Note: The data in brackets, [ ], represent the increase (+) in time to reach a selected point of temperature w.r.t the control sample.
Figure 6.18: Δt between the surface and back surface as a function of coating thickness at 180 and 250 °C for all samples at 35 and 50 kW/m² heat fluxes without an ignition source.
The slower rise in temperature at those heat fluxes can be clearly seen by the increase in time to reach the two selected temperatures in Table 6.9, where the time to reach the back surface temperature of 180 °C (softening) and 250 °C (onset of decomposition temperature of epoxy resin) are reported. The results in Table 6.9 (a) show that at 35 kW/m² with only the phenolic resin, the times to reach 180 and 250 °C of GRE composite could be delayed by 4 and 1 s, respectively. On one hand, the GRE-P/30B and GRE-P/Si samples, could be delayed by ~10-14 s for both temperature points. A similar delay in time to reach 180 and 250 °C was also observed in GRE-P/Flek. On the other hand, the Recoxit and zirconia coatings had a longer time delay (~15-18 s) to reach 180 and 250 °C than nanoclay, nanosilica and Flekashield coatings. With extra particles, the GRE-P/FlekS, GRE-P/ReS and GRE-P/ZrS samples show a further delay in time when compared to respective coated samples (see Table 6.9 (b)), especially in GRE-ReS and GRE-ZrS samples which could be delayed by more than 27 and 49 s to reach 180 °C, respectively, and more than 30 and 63 s to reach 250 °C of the GRE composite, while the GRE-P/FZrS sample shows a similar delay time to that observed in the nanoclay, nanosilica and Flekashield coated samples. At 50 kW/m², most ceramic particle-coated samples increased time-to-reach 180 and 250 °C by > 10 and >20 s respectively compared to the control sample, while GRE-P/ReS significantly increased time to reach 180 and 250 °C at the back surface by 30 and 56 s, respectively.

The effect of coating thickness on the thermal barrier efficiency of all ceramic particle coatings can be seen in Figure 6.18, where ΔT values, the difference between the surface and back surface temperatures at 180 and 250 °C are plotted as a function of coating thickness. The results indicate that the delay in temperature rise within the GRE composite structure strongly depends upon the thickness of the coatings. The Recoxit coating with additional particles provide the best thermal barrier performance in order to prevent the heat penetration from heat exposure surface to the underlying laminate at low and high heat fluxes compared with all other ceramic coatings.

6.3.5 Effect of the coatings on the mechanical properties of the composites

In order to study the effect of ceramic particle coatings on the mechanical properties of the composites, the GRE laminates with/without ceramic particle coatings were tested for their
impact and flexural behaviour using the impact drop weight and flexural three point bending tests. The experimental details are discussed in Section 3.8, Chapter 3.

6.3.5.1 Impact properties

A specimen size of 75 mm x 75 mm of each sample was tested using an impact drop weight test with a 4.62 kg steel impactor dropped from 110 mm height to produce an impact velocity of 1.46 m/s. The load-deflection curves of all samples are shown in Figure 6.19. The curves of load-deflection obtained under 5 J impact energies can be considered as the response of the composite materials to impact loads.

Figure 6.19: Load versus deflection curves of the control and coated samples from the 4.62 kg impactor and 110 mm drop height

In Figure 6.19, all samples exhibit both the loading and unloading portions of the curve due to the effect of clamping and vibration [18]. The loading, shown as the upper portion of the curve, implies that when the impactor hits the specimen, the lower portion of the curve represents the behaviour of specimen once the impactor rebounds from the specimen during the unloading process. For this type of curve (closed envelope), the impact modulus
(\(E_i\)) of each sample was calculated from the initial load - deflection curve before the rebound (see Section 3.8, Chapter 3). Moreover, in order to eliminate the effect of the difference of resin and glass fibre contents in the laminates, impact modulus for all the samples were normalised to 50% volume fraction of the glass fibre. The experimentally-measured and normalised impact moduli of all the samples values are given in Table 6.10.

Table 6.10: The impact moduli calculated for all GRE composite laminates at 5 J (4.62 kg drop weight with 110 mm drop height) energy level impact test

(a) Set I samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Glass fibre content</th>
<th>Coating thickness (µm)</th>
<th>Impact modulus (GPa)</th>
<th>Normalised impact modulus ** (GPa)</th>
<th>Change in modulus (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>58</td>
<td>39</td>
<td>-</td>
<td>12.6 ±0.4</td>
<td>16.0±0.3</td>
</tr>
<tr>
<td>GRE-Phe</td>
<td>60</td>
<td>41</td>
<td>120</td>
<td>13.2 ±0.8</td>
<td>16.0 ±0.7</td>
</tr>
<tr>
<td>GRE-P/30B</td>
<td>59</td>
<td>40</td>
<td>130</td>
<td>13.1 ±0.6</td>
<td>16.3±0.5</td>
</tr>
<tr>
<td>GRE-P/Si</td>
<td>60</td>
<td>41</td>
<td>100</td>
<td>13.7 ±0.6</td>
<td>16.6±0.5</td>
</tr>
<tr>
<td>GRE-P/Flek</td>
<td>59</td>
<td>40</td>
<td>270</td>
<td>12.4 ±1.1</td>
<td>15.4±0.9</td>
</tr>
<tr>
<td>GRE-P/Re</td>
<td>60</td>
<td>41</td>
<td>350</td>
<td>12.2 ±0.4</td>
<td>14.8±0.4</td>
</tr>
<tr>
<td>GRE-P/Zr</td>
<td>59</td>
<td>39</td>
<td>380</td>
<td>11.9 ±0.1</td>
<td>15.2±0.1</td>
</tr>
</tbody>
</table>

(b) Set II samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Glass fibre content</th>
<th>Coating thickness (µm)</th>
<th>Impact modulus (GPa)</th>
<th>Normalised impact modulus ** (GPa)</th>
<th>Change in modulus (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GRE-P/FlekS</td>
<td>60</td>
<td>41</td>
<td>280</td>
<td>11.9 ±0.7</td>
<td>14.4±0.5</td>
</tr>
<tr>
<td>GRE-P/ReS</td>
<td>58</td>
<td>39</td>
<td>630</td>
<td>7.5 ±0.3</td>
<td>9.6±0.2</td>
</tr>
<tr>
<td>GRE-P/ZrS</td>
<td>61</td>
<td>42</td>
<td>420</td>
<td>9.6 ±0.7</td>
<td>11.4±0.6</td>
</tr>
</tbody>
</table>

Note: % Change in modulus, (-) indicates reduction and (+) increase w.r.t to the value for the control; ** indicates the measured impact modulus value normalised to 50% volume fraction of the glass fibre; For glass fibre volume fraction calculation, the glass fibre density = 2.5 g/cm\(^3\), epoxy matrix density at 25 °C = 1.17 g/cm\(^3\)

As can be seen in Table 6.10, there is no clear trend in impact moduli of GRE composites with different ceramic particles coatings due to the variation of the glass fibre content in each laminate. The normalised results show that the presence of a 120 µm neat phenolic resin coating (GRE-Phe) shows a similar impact modulus to that shown by the control laminate, indicating that the thin coating of phenolic resin had no effect on the impact
modulus of the GRE laminate. The presence of nanoclay (GRE-P/30B) and nanosilica (GRE-P/Si) particles in the coatings have minimal detrimental effect on the impact modulus of coated samples. In fact, these samples showed an increase in the impact modulus of the GRE laminates by 1 and 3%, respectively, compared to the control sample. This is probably due to the presence of nanoparticles (nanoclay and nanosilica), which could act as a reinforcement to the phenolic resin binder in the coating leading to a stiffer coating on the substrate, and resulting in a slight increase in impact modulus of the composite. On the other hand, a decrease in the impact modulus was observed when Flekashield, Recoxit and zirconia particles were used in the coatings as GRE-P/Flek, GRE-P/Re and GRE-P/Zr which show 4, 8 and 6% reduction in modulus compared to the control sample, respectively. A further decrease was observed when an extra deposition of ceramic particles was applied to the coated surface, GRE-P/FlekS reduces the impact modulus of the GRE laminates by 10% compared to the control, GRE-P/ReS and GRE-P/ZrS reduce by 40 and 29%, respectively. These observations indicate that the presence of the thick coatings (>270 µm) containing large ceramic particle sizes (>40 µm, see Table 6.6) on the GRE laminate cause a negative effect on the impact property of the composite, and this negative effect is amplified when the concentration of those ceramic particles on the laminate surface is increased.

6.3.5.2 The effect of impact on the physical properties of the coatings

The effect of impact that can influence the morphology of the surface coatings was also examined in this section. After impact drop weight tests at 1 (Impactor 1.03 kg and 100 mm drop distance) and 5 J (Impactor 4.62 kg and 110 mm drop distance) impact energies, the morphologies of post-impact samples were examined using a digital camera with the aim of establishing the fractures of the coatings, such as cracking and debonding of the coatings due to the indentation stress from the impact. The area damaged by the drop test was analysed using Image J (analysis image software). The images and results are presented in Table 6.11.
Table 6.11: Images of impact damage and damaged observations on the front (impacted side) of all the GRE specimens after 1 J and 5 J drop-weight impact tests

(a) Set I samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>1 J Impact energy</th>
<th>Damaged observation and area (mm²)</th>
<th>5 J Impact energy</th>
<th>Damaged observation and area (mm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Images</td>
<td></td>
<td>Images</td>
<td></td>
</tr>
<tr>
<td>GRE-Phe</td>
<td>X</td>
<td>-</td>
<td>V</td>
<td>7.4 ± 1.2</td>
</tr>
<tr>
<td>GRE30B</td>
<td>X</td>
<td>-</td>
<td>C,D</td>
<td>21.9 ± 8.2</td>
</tr>
<tr>
<td>GRE-P/Si</td>
<td>X</td>
<td>-</td>
<td>V</td>
<td>9.7 ± 1.1</td>
</tr>
<tr>
<td>GRE-P/Flek</td>
<td>C,D</td>
<td>14.7 ± 2.6</td>
<td>C,D</td>
<td>51.8 ± 11.1</td>
</tr>
<tr>
<td>GRE-P/Re</td>
<td>X</td>
<td>-</td>
<td>C,D</td>
<td>45.3 ± 8.3</td>
</tr>
<tr>
<td>GRE-P/Zr</td>
<td>C</td>
<td>11.5 ± 0.9</td>
<td>C,D</td>
<td>30.0 ± 7.8</td>
</tr>
</tbody>
</table>

(b) Set II samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>1 J Impact energy</th>
<th>Damaged observation and area (mm²)</th>
<th>5 J Impact energy</th>
<th>Damaged observation and area (mm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Images</td>
<td></td>
<td>Images</td>
<td></td>
</tr>
<tr>
<td>GRE-P/FlekS</td>
<td>C,D</td>
<td>20.2 ± 2.6</td>
<td>C,D</td>
<td>33.4 ± 5.4</td>
</tr>
<tr>
<td>GRE-P/ReS</td>
<td>X</td>
<td>-</td>
<td>C,D</td>
<td>10.6 ± 1.6</td>
</tr>
<tr>
<td>GRE-P/ZrS</td>
<td>C,D</td>
<td>17.0 ± 1.5</td>
<td>C,D</td>
<td>38.9 ± 5.2</td>
</tr>
</tbody>
</table>

Note: X: no damage appears, V: visible surface damage (The coating is damaged by impact tup at a local area), D: debonding of coating and C: cracking of coating
The results show that with the phenolic resin coating (GRE-Phe) without particles there was no surface damage observed from the 1 J impact. However, under higher energy impacts (5 J), larger visible surface damage was observed. Similarly, there was no damage at 1 J and some surface fractures observed at 5 J impact conditions for GRE-P/Si and GRE-P/30B samples. For the Flekashield coating, in GRE-P/Flek sample, cracking and/or debonding of the coating from the 1 J impact (see Table 6.11) can be observed, which is further amplified when additional particles are applied in GRE-P/FlekS. At 5 J impact, a larger damage area which appears to be a combination of debonding and cracking of the coating, was observed for both Flekashield coated samples (GRE-P/Flek and GRE-P/FlekS) compared to that observed at 1 J impact. In the cases of the Recoxit and zirconia particle coatings, the GRE-P/Re displays the surface without any damage at 1 J, similar to that observed in the GRE-P/ReS sample, while, both Recoxit-coated samples (GRE-P/Re and GRE-P/ReS) suffer from cracking and/or debonding of the coating from the 5 J impact, which indicates that increasing particles on the surface of Recoxit coatings did not have much effect on the impact drop weight test. GRE-P/Zr and GRE-P/ZrS samples had similar cracking and/or debonding behaviour of the coating to that of Flekashield coated samples. The zirconia coating could not sustain the load at 1 J impact energy, and on increasing particle concentration (GRE-P/ZrS) can give rise to various fractures as clearly seen in Table 6.11. These results indicate that apart from a neat phenolic resin, only the nanosilica coating (containing 10 wt% of particles) showed resilience to the 5 J drop test, due to the lower level of particles in the coating relative to the other samples. All other samples due to higher particulate levels show signs of being more brittle in nature and hence fracture more readily under impact.

6.3.5.3 Flexural properties

In order to study the effect of the ceramic particle surface coatings on the flexural property of GRE laminates, all the samples (size 125 mm x 13 mm) were tested for their flexural performance in the three point bending mode (see Section 3.8.3, Chapter 3). Load-displacement curves for all samples obtained from three point bending tests are shown in Figure 6.20 and their flexural moduli were calculated using the Engineers’ bending theory as discussed in Section 3.8.2 (Chapter 3). To eliminate the effect of the difference in resin and glass fibre contents of each laminate, the experimentally-measured flexural modulus of
all the samples were normalised similar to that used in Section 6.3.5.1. The experimentally-measured and normalised impact moduli of all the samples are given in Table 6.12.

![Figure 6.20: Load versus extension curves of the control and coated samples at room temperature from three point bending tests](image-url)

**Table 6.12: The flexural moduli of the control and coated GRE laminates**

(a) Set I samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Glass fibre content</th>
<th>Coating thickness</th>
<th>Flexural modulus</th>
<th>Normalised flexural modulus</th>
<th>Change in modulus (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>59 wt% 40 vol%</td>
<td>-</td>
<td>15.1±0.8</td>
<td>18.8±0.7</td>
<td>-</td>
</tr>
<tr>
<td>GRE-Phe</td>
<td>61 wt% 42 vol%</td>
<td>130 ± 0</td>
<td>14.9±0.3</td>
<td>17.6±0.2</td>
<td>-6</td>
</tr>
<tr>
<td>GRE-P/30B</td>
<td>57 wt% 38 vol%</td>
<td>150 ±10</td>
<td>13.2±0.6</td>
<td>17.2±0.7</td>
<td>-8</td>
</tr>
<tr>
<td>GRE-P/Si</td>
<td>60 wt% 41 vol%</td>
<td>110 ± 0</td>
<td>14.6±0.9</td>
<td>17.7±0.8</td>
<td>-6</td>
</tr>
<tr>
<td>GRE-P/Flek</td>
<td>59 wt% 40 vol%</td>
<td>290 ± 0</td>
<td>13.4±0.1</td>
<td>16.6±0.1</td>
<td>-11</td>
</tr>
<tr>
<td>GRE-P/Re</td>
<td>63 wt% 41 vol%</td>
<td>360 ±10</td>
<td>13.6±0.4</td>
<td>16.7±0.4</td>
<td>-12</td>
</tr>
<tr>
<td>GRE-P/Zr</td>
<td>62 wt% 43 vol%</td>
<td>490 ±10</td>
<td>12.6±0.4</td>
<td>14.6±0.3</td>
<td>-22</td>
</tr>
</tbody>
</table>

(b) Set II samples
<table>
<thead>
<tr>
<th>Sample</th>
<th>Glass fibre content</th>
<th>Coating thickness</th>
<th>Flexural modulus</th>
<th>Normalised flexural modulus</th>
<th>Change in modulus</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mass (wt%)</td>
<td>Volume fraction (vol%)</td>
<td>(µm)</td>
<td>(GPa)</td>
<td></td>
</tr>
<tr>
<td>GRE-P/FlekS</td>
<td>58</td>
<td>39</td>
<td>340 ±20</td>
<td>12.8±0.2</td>
<td>-13</td>
</tr>
<tr>
<td>GRE-P/ReS</td>
<td>60</td>
<td>41</td>
<td>630 ±30</td>
<td>9.6±0.5</td>
<td>-38</td>
</tr>
<tr>
<td>GRE-P/ZrS</td>
<td>58</td>
<td>39</td>
<td>510 ±40</td>
<td>10.6±0.9</td>
<td>-28</td>
</tr>
</tbody>
</table>

Note: % Change in modulus, (-) indicates reduction and (+) increase w.r.t respective value for the control; ** indicates the measured impact modulus value normalised to 50% volume fraction of the glass fibre

The results in Table 6.12 show that the normalised flexural moduli of all coated samples are lower than that of the control laminate. The presence of a 130 µm neat phenolic resin coating reduces the flexural modulus of the GRE laminates by 5% compared to the control sample. This is due to the flexural modulus of the phenolic resin being lower than the epoxy resin matrix in the composite. Therefore, the overall flexural modulus of the coated sample was reduced [19,20]. When the ceramic particles were added into the coating, a general reduction in flexural modulus is observed depending upon the nature of the coating. In comparison to the control, the nanosilica particle coating (GRE-P/Si) shows similar reduction in flexural modulus to that in sample GRE-Phe, while, the decrease in the flexural modulus was more pronounced when nanoclay, Flekashield, Recoxit and zirconia particles were used in the coatings. GRE-P/30B, GRE-P/Flek, GRE-P/Re and GRE-P/Zr show 8, 11, 12 and 22 % reduction in flexural modulus compared to the control sample, respectively. This observation suggests that the effect of coating on the flexural modulus of the GRE composite is minimised in the case of nanosilica, which is probably due to the lowest particle deposition of nanoscale silica particles in the coatings and the very thin coating of GRE-P/Si compared to other coated samples (see Table 6.12). Considering the effect of the extra deposition of ceramic particles, the negative effect on the flexural modulus of the GRE laminates is amplified compared to the normal ceramic particle coatings. With respect to the control, the additional particle depositions and coating thickness of Flekashield, Recoxit and Zirconia coatings reduced the flexural modulus of GRE composite by 13 % for GRE-P/FlekS, 38 % for GRE-P/ReS and 28 % for GRE-P/ZrS. This suggests that increasing coating thickness reduces the flexural modulus of the GRE composite. Therefore, it can be concluded that the effect of ceramic particle coatings on flexural modulus of GRE composite is dependent upon the amount of the particle deposition on the surface used and the thickness of the coatings.
6.3.6 Flexural performance after exposure to different heat flux conditions

The effect of radiant heat on the mechanical properties of the GRE composites was investigated by exposing samples to a cone heater (cone calorimeter) at different heat fluxes and then measuring the residual flexural modulus of the samples by the three point-bending test (see Section 3.8.3 (Chapter 3)). The flexural load was applied on the heat-damaged surface so that the damaged surface would bear the compressive strain. While calculating the residual flexural modulus, the original thickness of the sample was used. There was no significant difference in the thickness after heat exposure and that obtained at room temperature (prior to heat exposure). The flexural modulus and percentage retention of this measure for all post-heat exposure samples are reported in Table 6.13. Digital images for all post-heat exposure samples after the three point-bending tests were also studied to invest their structure integrity and presented in Figure 6.21.

The results in Table 6.13 and Figure 6.21 show that when the laminates were exposed to a 25 kW/m² heat flux for 60 s, there was no significant damage to the structure, only the top surfaces of all laminates are slightly charred. As expected, there is no significant difference between modulus retention of the control and coated samples. However, when the exposure time was increased to 120 s, the control and GRE-Phe samples showed only ~50 % flexural modulus retention. On the other hand, all ceramic particle coatings showed higher retentions in flexural modulus compared to the control sample. GRE-P/30B, GRE-P/Si, GRE-P/Flek, GRE-P/Re and GRE-P/Zr samples retain ~ 80% of the original flexural modulus of the control laminate. In the case of additional ceramic particles on the coating, the modulus retention of the laminate is 89 % for GRE-P/FlekS, 93 % for GRE-P/ReS and 84 % for GRE-P/ZrS (see Table 6.13). These results indicate that the use of these ceramic particles in the coatings provide a thermal barrier protection to the underlying laminate and help in preserving the flexural property of GRE composite laminate when exposed to 25 kW/m² heat flux for 120 s, and the thermal barrier efficiency depends upon the coating thickness. The additional particles enhances the thermal barrier protection of the coatings. This observation is consistent with the results in Figure 6.21, where the control and GRE-Phe samples show a significant loss in the structural integrity of the laminate after exposure to 25 kW/m² heat flux for 120 s. Although all the ceramic-coated samples showed some degree of delamination (glass fibres torn apart from the laminate structure), the damage is not to the same extent as in control and GRE-Phe samples due to the thermal barrier...
protection afforded by the ceramic particle coatings, especially, GRE-P/ReS which shows a good degree of structure integrity. As the exposure time was increased to 240 s, all ceramic particle coatings could not retain the structural integrity property of GRE composite. Less than 20% retention in flexural modulus (Table 6.13), severe delamination and loss in structural integrity of the composite laminate can be clearly seen from Figure 6.21.

![Digital images (side-view) showing damaged area after three point bending tests of the control and coated samples exposed to 25 and 50 kW/m² heat fluxes](image_url)

**Figure 6.21**: Digital images (side-view) showing damaged area after three point bending tests of the control and coated samples exposed to 25 and 50 kW/m² heat fluxes
Table 6.13: The flexural modulus and % modulus retention of the control and all coated samples after exposure to radiant heat of 25 and 50 kW/m² heat fluxes for different times

(a) Set I samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Post-Exposure to 25 kW/m²</th>
<th>Post-Exposure to 50 kW/m²</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>60 s</td>
<td>120 s</td>
</tr>
<tr>
<td></td>
<td>Modulus (E_f) % E_f retention</td>
<td>Modulus (E_f) % E_f retention</td>
</tr>
<tr>
<td>Control</td>
<td>15.0±0.9 94±1</td>
<td>7.1±2.4 47±11</td>
</tr>
<tr>
<td>GRE-Phe</td>
<td>13.5±0.1 92±1</td>
<td>9.0±0.2 56±2</td>
</tr>
<tr>
<td>GRE-P/30B</td>
<td>12.8±0.0 94±1</td>
<td>10.4±0.2 81±2</td>
</tr>
<tr>
<td>GRE-P/Si</td>
<td>15.2±0.3 94±1</td>
<td>13.2±0.8 84±1</td>
</tr>
<tr>
<td>GRE-P/Flek</td>
<td>12.5±0.1 93±1</td>
<td>11.5±1.7 85±8</td>
</tr>
<tr>
<td>GRE-P/Re</td>
<td>13.4±0.2 90±1</td>
<td>12.5±1.5 81±5</td>
</tr>
<tr>
<td>GRE-P/Zr</td>
<td>12.1±0.7 93±2</td>
<td>10.2±0.0 82±6</td>
</tr>
</tbody>
</table>

(b) Set II samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Post-Exposure to 25 kW/m²</th>
<th>Post-Exposure to 50 kW/m²</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>60 s</td>
<td>120 s</td>
</tr>
<tr>
<td></td>
<td>Modulus (E_f) % E_f retention</td>
<td>Modulus (E_f) % E_f retention</td>
</tr>
<tr>
<td>GRE-P/FlekS</td>
<td>12.1±0.1 94±1</td>
<td>11.2±0.2 89±1</td>
</tr>
<tr>
<td>GRE-P/ReS</td>
<td>9.3±0.2 95±1</td>
<td>9.0±1.1 93±1</td>
</tr>
<tr>
<td>GRE-P/ZrS</td>
<td>9.9±1.0 91±2</td>
<td>8.7±0.8 84±3</td>
</tr>
</tbody>
</table>
The % flexural modulus retentions of all samples are plotted as a function of exposure time at 25 kW/m$^2$ heat flux, in Figure 6.22. The results show that the flexural modulus of the GRE laminate reduces on exposure to heat. The reduction is amplified with increase in exposure time. However, the reduction in the modulus was retarded when the ceramic particle coatings were applied on the GRE laminate, especially in cases where additional ceramic particles were applied on surfaces of the coatings.

Figure 6.22: Flexural modulus retention of the control and coated samples after exposure to 25 kW/m$^2$ heat flux for different times

As heat flux was increased to 50 kW/m$^2$, after 30 s exposure time, the control and GRE-Phe could retain only ~ 70% flexural modulus, while GRE-P/30B, GRE-P/Si, GRE-P/Flek, GRE-P/Re and GRE-P/Zr samples can retain 80-90% of the original flexural modulus of the control laminate (see Table 6.13). With additional ceramic particles the GRE-P/FlekS, GRE-P/ReS and GRE-P/ZrS samples retain a higher flexural modulus (89
% for GRE-P/FlekS, 99 % for GRE-P/ReS and 85 % for GRE-P/ZrS) than those with normal respective ceramic particle coatings. These results can be corroborated with the images in Figure 6.21, which show that only the control and GRE-Phe display a noticeable degree of heat damage in the composite structure, whereas all coated samples show only damage in the top surface. This indicates that at higher heat flux the ceramic particle coatings can provide thermal barrier protection to the GRE composites, but only for a short period of time.

From the flexural modulus retention results, it can be concluded that the coating of Recoxit (GRE-P/ReS) sample performed the best to protect the underlying laminate from the heat as can be seen it has the lowest reduction in flexural moduli at all heat exposure conditions. These results can also be related to the thermal barrier results in Section 6.3.4, showing that all coated samples show significantly delayed temperature rise at the back surface (un-exposed) compared to the control sample at 35 and 50 kW/m² heat fluxes, especially in GRE-P/ReS and GRE-P/ZrS.

6.3.7 Durability of coatings

The durability to water and peeling of the ceramic particle coatings using this phenolic resin binder was tested according to Section 3.9 in Chapter 3 and the results are discussed below.

6.3.7.1 Effect of water on ceramic particle coatings

The effect of water on the durability of these ceramic particle coatings was investigated using the water-soak test. In this experiment, all edges were sealed with an epoxy resin prior to the test to avoid the water absorption into the laminated structure. The images and change in weight (wt%) before and after the test are reported in Table 6.14.
Table 6.14: The digital images of all GRE surfaces before and after the water-soak test and weight loss (wt%) after the test

(a) Set I samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Images</th>
<th>% Weight loss after 24 h soaking in water and 24 h drying at RT</th>
<th>% Weight loss after drying at RT</th>
<th>% Weight loss after drying at 100°C for 2h</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>-</td>
<td>-</td>
<td>-0.06 ±0.01</td>
<td>-0.07 ±0.02</td>
</tr>
<tr>
<td>GRE-P/30B</td>
<td>-</td>
<td>-</td>
<td>-0.03 ±0.01</td>
<td>-0.12 ±0.03</td>
</tr>
<tr>
<td>GRE-P/Si</td>
<td>-</td>
<td>-</td>
<td>-0.05 ±0.01</td>
<td>-0.12 ±0.01</td>
</tr>
<tr>
<td>GRE-P/Flek</td>
<td>-</td>
<td>-</td>
<td>-0.03±0.03</td>
<td>-0.10 ±0.05</td>
</tr>
<tr>
<td>GRE-P/Re</td>
<td>-</td>
<td>-</td>
<td>-0.03 ±0.01</td>
<td>-0.09 ±0.06</td>
</tr>
<tr>
<td>GRE-P/Zr</td>
<td>-</td>
<td>-</td>
<td>-0.04 ±0.01</td>
<td>-0.17 ±0.02</td>
</tr>
</tbody>
</table>

(b) Set II samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Images</th>
<th>% Weight loss after 24 h soaking in water and 24 h drying at RT</th>
<th>% Weight loss after drying at RT</th>
<th>% Weight loss after drying at 100°C for 2h</th>
</tr>
</thead>
<tbody>
<tr>
<td>GRE-P/FlekS</td>
<td>-</td>
<td>-</td>
<td>-0.08 ±0.01</td>
<td>-0.17 ±0.04</td>
</tr>
<tr>
<td>GRE-P/ReS</td>
<td>-</td>
<td>-</td>
<td>-0.04 ±0.01</td>
<td>-0.12 ±0.05</td>
</tr>
<tr>
<td>GRE-P/ZrS</td>
<td>-</td>
<td>-</td>
<td>-0.06 ±0.01</td>
<td>-0.17 ±0.07</td>
</tr>
</tbody>
</table>
The results in Table 6.14 show that after the water-soak test for 24 h and drying the samples at room temperature for 24 h, all the coated samples had minimal weight loss, (~0.03-0.08 %). Subsequently, after drying in an oven at 100 °C, only a very small further weight loss was observed. These weight loss results are comparable to those of the control sample and are within the experimental error range. The images before and after test also show that there is no significant change in surface morphology of all the coated samples, i.e. there is no significant removal of the particles from the coated layer after the test.

6.3.7.2 Adhesion between coatings and GRE surfaces

The adhesion between these ceramic particle coatings and GRE composite substrate was evaluated using a tape pull test (Section 3.9.2, Chapter 3).

Table 6.15: The changes in weight after the tape pull test from different areas of the coated samples

(a) Set I samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Thickness of coating (µm) and % coating deposition</th>
<th>Images of the tapes after tape pull test</th>
<th>% Total weight loss</th>
<th>% Peeling of the coating</th>
</tr>
</thead>
<tbody>
<tr>
<td>GRE-P/30B</td>
<td>130, 4.5 %</td>
<td></td>
<td>0.01 ±0.01</td>
<td>-</td>
</tr>
<tr>
<td>GRE-P/Si</td>
<td>110, 2.0 %</td>
<td></td>
<td>0.02 ±0.01</td>
<td>-</td>
</tr>
<tr>
<td>GRE-P/Flek</td>
<td>280, 5.4 %</td>
<td></td>
<td>0.03 ±0.01</td>
<td>-</td>
</tr>
<tr>
<td>GRE-P/Re</td>
<td>350, 12.2 %</td>
<td></td>
<td>0.02 ±0.01</td>
<td>-</td>
</tr>
<tr>
<td>GRE-P/Zr</td>
<td>470, 17.9 %</td>
<td></td>
<td>0.03 ±0.01</td>
<td>-</td>
</tr>
</tbody>
</table>
In Table 6.15, the results of % weight loss and % coating peeled after test for all the coated samples are reported. The digital images of the tapes after the peeling test are also shown in this table. The results in Table 6.15 show that all the coated samples without any extra deposition of ceramic particles did not peel off when subjected to a tape test. Even in samples with additional particles, the % coating peeling is minimal. These observations indicate that the use of a phenolic resin binder (≥ 30 wt%) helps in the permanent deposition of a high-concentration of ceramic particles on a GRE laminate surface. Where additional ceramic particles were applied to the coated surface following application of the ceramic-phenolic suspension coating, GRE-P/FlekS, GRE-P/ReS and GRE-P/ZrS show a very small removal of the ceramic particles (0.98, 0.53 and 0.34 %, respectively) but overall, the coating is quite stable and does not peel off.

### 6.3.8 Conclusions

This work has shown that nanoclay, nanosilica, Flekashield, Recoxit and zirconia particles can be uniformly dispersed in a resin and coated on the GRE composite surfaces. Additional ceramic particles can be placed on the coating by dry sieving to improve the loading of ceramic particles upon the GRE composite surface. In terms of the thermal barrier properties, all ceramic particles showed good performance. On exposure to 35 and
50 kW/m² heat fluxes, the coatings were very effective in increasing TTI of composite, due to the combination of ceramic particles and the inherently flame retardant properties of the phenolic resin binder in the coating. The coatings could reduce PHRR and increase $T_{PHRR}$. The additional ceramic particles amplified the thermal barrier effect of the ceramic coatings. The best performance was shown by Flekashield coatings. In terms of heat penetration, all ceramic coatings delayed the rise in temperature at back surface of the sample, increasing times-to-reach 180 °C and 250 °C of the laminate. GRE-P/ReS observed the slowest increase in temperature compared to the other coated samples, as it had the highest coating thickness. It is worth pointing out that the thermal barrier efficiency of each ceramic particle is strongly dependent on the concentration of particles on the substrate and the coating thickness. If the surface is completely covered by ceramic particles, it is expected that the coating will provide an effective thermal barrier protection to the GRE composite.

In terms of mechanical properties, almost all the ceramic coatings slightly decreased the impact and flexural moduli of the GRE composite, but the reduction is not significant. The additional ceramic particles on the coated surface reduced the impact and flexural moduli. However, all ceramic particle coatings could preserve the flexural property of GRE composites after exposure to 25 kW/m² heat flux for 120 s and 50 kW/m² heat flux for 30 s. In terms of durability, although all ceramic coatings are durable to peeling and to the water soak test, they could not withstand the impact test and cracked /debonded.

*Effect of resin binder on the coating*

In Part I and III, the ceramic particles were used to prepare the ceramic particle coatings (70:30 ratio of Ceramic:Resin) using different application methods and resin binders (see Section 6.1.1 and 6.3.1). In both sets, Recoxit and zirconia have been used, hence only these two have been used for comparison of the two resin binders and the application methods used. The coating thickness, % particle deposition, $\Delta$ parameter (TTI, PHRR and $T_{PHRR}$) of the each coated sample w.r.t the control sample (at 30 kW/m² for the flame retarded epoxy binder set and 35 kW/m² for phenolic binder set) and SEM images are summarised in Table 6.16.
Table 6.16 (a): Comparison of physical properties of the ceramic particle coatings using the flame retarded epoxy and phenolic resin binders

<table>
<thead>
<tr>
<th>Sample</th>
<th>Resins and application methods</th>
<th>SEM (1000X)</th>
<th>Coating thickness (µm)</th>
<th>% Particle deposited (w.r.t laminate)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GRE-DP/Re</td>
<td>DOPO flame retarded epoxy resin (paint brush and roller)</td>
<td></td>
<td>890 ± 60</td>
<td>34 ± 1</td>
</tr>
<tr>
<td>GRE-DP/Zr</td>
<td></td>
<td></td>
<td>940 ± 210</td>
<td>38 ± 3</td>
</tr>
<tr>
<td>GRE-P/Re</td>
<td>Phenolic resin (K-bar coater)</td>
<td></td>
<td>345 ± 30</td>
<td>10 ± 1</td>
</tr>
<tr>
<td>GRE-P/Zr</td>
<td></td>
<td></td>
<td>469 ± 48</td>
<td>14 ± 1</td>
</tr>
</tbody>
</table>

Table 6.16 (b): Comparison of flammability of the ceramic particle coatings using the flame retarded epoxy and phenolic resin binders

<table>
<thead>
<tr>
<th>Sample</th>
<th>30 kW/m² with ignition source</th>
<th>Sample</th>
<th>35 kW/m² without ignition source</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ΔTTI (s)</td>
<td>ΔPHRR (kW/m²)</td>
<td>ΔT PHRR (s)</td>
</tr>
<tr>
<td>GRE-DP/Re</td>
<td>+6</td>
<td>-113</td>
<td>+36</td>
</tr>
<tr>
<td>GRE-DP/Zr</td>
<td>-1</td>
<td>-101</td>
<td>+38</td>
</tr>
</tbody>
</table>

On comparing the application method of paint brushing in Part I and the use of a K-bar coater in Part III, it can be seen that the latter (K-bar coating) reduces the coating thickness and % ceramic particle deposition. With the K-bar coating method there is a
better dispersion and particle distribution on GRE laminate surfaces, as clearly seen from Table 6.16 (a).

Different heat flux conditions were used in Parts I and III. In Part I, an ignition source was used, while in Part III an ignition source was not used. Hence, the direct comparison of the thermal barrier effectiveness between these two different coating sets cannot be carried out. However, Δ TTI and PHRR parameters with respect to the respective control samples demonstrate the effect of the binder in the coatings. The results in Table 6.16 (b) show that phenolic resin binder increased time-to-ignition of the coated samples (i.e. GRE-P/Re and GRE-P/Zr), whereas DOPO flame retarded epoxy resin did not (i.e. GRE-EP/Re and GRE-EP/Zr). The DOPO containing epoxy resin, however, had more effect on reducing PHRR than the phenolic resin binder. However, both binders helped in increasing $T_{\text{PHRR}}$ of the coated samples compared to the control samples.

6.4 References


Chapter 7

CHEMICAL COATING

This chapter discusses the effect of a chemical coating on the physical fire and mechanical properties of GRE laminates. Vinyl phosphonic acid (VPA) monomers in presence of a crosslinking agent (trialllyl isocyanurate, TAICROS®) and a photo-initiator (2-hydroxy-2-methylpropophenone, Darocur1173) were polymerised on GRE composite laminate surfaces via a UV photo-polymerisation reaction, as discussed in Section 3.5 (Chapter 3). Samples with two coating thicknesses (300 and 500 µm) of poly (vinyl phosphonic acid) (PVPA) coatings were prepared. The PVPA coated surface was characterised by SEM and IR-ATR. The flammability, thermal barrier properties, durability and mechanical properties of these coated samples have been studied.

7.1 Physical properties of the coatings

Table 7.1: Physical properties of the coating, referring to the amount applied on a 75 mm x 150 mm plaque of the GRE laminates

<table>
<thead>
<tr>
<th>Sample</th>
<th>Coating thickness (µm)</th>
<th>Mass of coating (g)</th>
<th>% PVPA coating deposition (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GRE-0.3PVPA</td>
<td>360 ±20</td>
<td>7.0 ±0.3</td>
<td>17.4 ±1.3</td>
</tr>
<tr>
<td>GRE-0.5PVPA</td>
<td>570 ±60</td>
<td>12.8 ±0.9</td>
<td>26.2 ±2.9</td>
</tr>
</tbody>
</table>

In Table 7.1, the thickness of each coating and the % PVPA coating deposition are reported. The results in Table 7.1 show that with ~360 µm thick coating, 17.4 wt% and with 570 µm coating, 26.2 wt% PVPA was deposited.
7.2 Surface characterisation

7.2.1 Scanning electron microscopy (SEM)

The morphology PVPA-coated samples was characterised by scanning electron microscopy (SEM).

The results in Figure 7.1 show that after VPA polymerisation in samples GRE-0.3PVPA and GRE-0.5PVPA, a rougher and scaler surface was observed, compared to the smooth surface observed in the control sample (see Figure 7.1 (a - f)). The PVPA coatings are uniform and completely cover the surface, indicating a uniform, polymerised PVPA film.
covering the whole GRE surface. The increase in coating thickness has no further effect on the roughness of the surfaces.

7.2.2 Infrared spectroscopy (IR) of the surfaces

The thin film of poly (vinyl phosphonic acid) (PVPA) prepared on a sheet of grease proof paper, similar to the coatings on the GRE composite surface, was characterised by IR-ATR. The transmittance IR traces of VPA monomer, crosslinker, PVPA film are shown in Figure 7.2. The IR-ATR of the control laminate and VPA polymerised on the laminate’s surface are shown in Figure 7.3.

![Figure 7.2: IR spectra of (a) triallyl isocyanurate crosslinker, (b) VPA monomer and (c) PVPA thin film](image)

From Figure 7.2 (b), the characteristic peaks of VPA monomer can be identified as: bands at 1040–890 cm\(^{-1}\): a symmetric stretching vibrations of P-OH group; 1115 cm\(^{-1}\): P=O stretching of the phosphonic acid; 1405 cm\(^{-1}\): vinyl C-H in plane bending; 1614 cm\(^{-1}\): C=C band of the allyl phosphonic acid and broad bands with medium intensity at 2850-2750 and 2500-2300 cm\(^{-1}\): P-O-H group [1,2,3]. In Figure 7.2 (c), all characteristic peaks of the VPA monomer can be seen in the PVPA thin film, suggesting that the phosphoric acid group of the PVPA units is preserved during the photo-polymerisation. The absence
of the C=C band at 1614 cm\(^{-1}\), and the appearance of saturated aliphatic C-H bending and stretching at 2922 and 2852 cm\(^{-1}\) in the PVPA spectrum is indicative of the increase in C-C bonds during the polymerisation reaction. Moreover, crosslinking between VPA polymer chains and the triallyl isocyanurate in PVPA film is indicated by the new peaks at 1459 cm\(^{-1}\) corresponding to C-H stretching and 1662 cm\(^{-1}\) representing C=O stretching vibrations, both of which are the characteristic peaks of triallyl isocyanurate [4,5], as seen in Figure 7.2 (a and c).

As compared to the control sample, the GRE-PVPA sample is very different. In the latter, all the characteristic peaks of epoxy resin [6], such as aromatic C-H (1606 and 1509 cm\(^{-1}\)), aromatic ring stretching (1583 and 1450 cm\(^{-1}\)), C-O (1110 and 1080 cm\(^{-1}\)) and epoxy ring (1241 cm\(^{-1}\)) are replaced by the peaks representing PVPA coating, which indicates that the coating completely covers the GRE composite surface (see Figure 7.3). It should be noted that this study only characterises the surface of the coated samples, and does not give any information about the chemical bonding between the coating and the epoxy resin of the substrate.

**Figure 7.3: IR spectra of (a) the control laminate and (b) GRE-PVPA**
7.3 Mechanism of photo-polymerisation of poly (vinyl phosphonic acid) (PVPA)

Based on the IR spectra results discussed above, a possible mechanism of polymerisation of VPA can be proposed as shown in Figure 7.4. The photo-induced radical polymerisation starts by UV-irradiation in the presence of the photo-initiator (Darocur 1173). This photo-initiator is decomposed to produce two initiating free radicals. The free radicals attack the VPA monomer molecule to form an active monomer as demonstrated in Figure 7.4 (a). Following the photo-initiation step, the active monomer attacks other monomers, forming active dimers, trimers etc. This process keeps repeating and many more monomers are successively added to a growing chain forming an active long chain (see Figure 7.4 (b-1). In parallel, the active monomers can also attack triallyl isocyanurate (crosslinker) molecules, initiating another chain reaction, crosslinking triallyl isocyanurate with VPA growing chains and forming a three dimensional network (see Figure 7.4 (b-2). In principle, any two radicals in the radically-induced polymerisation system can combine to give an inactive product. Therefore, the VPA growing chains are terminated at some point when the active chain centre is destroyed by an appropriate reaction depending on the type of reactive centre and the particular reaction conditions, such as combination or disproportionation reactions. In Figure 7.4 (c), the simple possible termination steps are illustrated as (1) a combination reaction, which is a joining of the two long chains with an active radical (—CH●) to give a poly (vinyl phosphonic acid) and (2) a disproportionation reaction to give two terminated chains, one with an unsaturated carbon group and the other fully saturated.
Figure 7.4: Possible mechanism of photo-polymerisation of VPA; (a) photo-initiation step, (b) propagation step and (c) termination steps
7.4 Flammability behaviour of GRE composites with PVPA chemical coatings

The flammability behaviour of GRE composite laminates with/without PVPA coatings was evaluated by the cone calorimeter at 35 and 50 kW/m$^2$ without an ignition source. The HRR vs. time curves of the control and coated samples are shown in Figure 7.5 while the extracted numerical data are presented in Table 7.2. Also, the mass loss rate vs. time curves of the control and all coated samples are shown in Figure 7.6. At 35 kW/m$^2$, the control sample ignited after 110 s of continued exposure to the heat without spark ignition. Figure 7.5 shows a sharp and intense single peak of HRR of 504 kW/m$^2$ at 141 s. The process of heat release from the control sample finished within 270 s (see Table 7.2). At the end of the test, all the resin was burnt, and only layers of glass fabric were left as shown in Table 7.3. With PVPA coatings of 320 and 510 µm thicknesses, Figure 7.5 (a-b), all three replicates of GRE-0.3PVPA and GRE-0.5PVPA samples show a flat line of the HRR curve indicating the samples did not ignite and burn. This results in a minimal heat release rate in both PVPA-coated samples. There is no obvious PHRR for GRE-0.3PVPA and GRE-0.5PVPA. Hence, all the PVPA coated samples observed a very low total heat release rate (THR) values, which is 1.2 MJ/m$^2$ for GRE-0.3PVPA and 0.9 MJ/m$^2$ for GRE-0.5PVPA. Besides, a significant reduction in mass loss rate was also observed for all PVPA-coated samples compared to the control sample as seen in Figure 7.6 (a). These results clearly demonstrate the superior flame retardant and thermal barrier efficacy of the PVPA coating, protecting the underlying composite substrate from heat/fire and severe burning. The PVPA coating produced an expanded char, which protected the underlying composite from heated/fire, resulting in no ignition. This char slows down the decomposition of the epoxy resin in the composite by acting as barrier to heat to the underlying substrate and diffusion of volatile combustible product from the substrate to the surface [7]. As can be seen from the images of the char residues at the end of the test in Table 7.3 that the 320 µm of PVPA coating formed a 28.7 mm thick char, while 510 µm thick coating (GRE-0.5PVPA) provided a 32 mm thick char layer. The expansion ratio of 320 µm was 96, while for 520 µm thick, it was only 64 (Table 7.3), indicating that the char expansion ratio decreases with increasing coating thickness.
Figure 7.5: HRR versus time curves of the control and coated samples at 35 and 50 kW/m² heat fluxes without an ignition source
[* indicates that the sample did not ignite]
Table 7.2: Cone calorimetric data for the control and all coated samples at 35 and 50 kW/m² heat fluxes without an ignition source

<table>
<thead>
<tr>
<th>Heat flux (kW/m²)</th>
<th>Sample</th>
<th>Specimen No.</th>
<th>Coating thickness (µm)</th>
<th>TTI (s)</th>
<th>Flame out time (s)</th>
<th>PHRR (kW/m²)</th>
<th>T_{PHRR} (s)</th>
<th>THR (MJ/m²)</th>
<th>FIGRA (kW/m²s)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>35</strong></td>
<td>Control 1,2,3T</td>
<td>-</td>
<td>110±2</td>
<td>270±4</td>
<td>504 ±12</td>
<td>141 ±13</td>
<td>35.7 ± 2.3</td>
<td>3.60 ±0.36</td>
<td></td>
</tr>
<tr>
<td>GRE-0.3PVPA 1*,2*,3T*</td>
<td>320 ±20</td>
<td>-</td>
<td>-</td>
<td>8 ±2</td>
<td>259 ±29</td>
<td>1.2 ± 0.6</td>
<td>0.03 ±0.01</td>
<td></td>
<td></td>
</tr>
<tr>
<td>GRE-0.5PVPA 1*,2*,3T*</td>
<td>510 ±30</td>
<td>-</td>
<td>-</td>
<td>6 ±1</td>
<td>221 ±66</td>
<td>0.9 ± 0.8</td>
<td>0.03 ±0.01</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>50</strong></td>
<td>Control 1,2,3T</td>
<td>-</td>
<td>60 ±2</td>
<td>196±10</td>
<td>572 ±33</td>
<td>99 ±13</td>
<td>42.2 ±1.7</td>
<td>5.91 ±0.95</td>
<td></td>
</tr>
<tr>
<td>GRE-0.3PVPA 1, 3T</td>
<td>320 ±10</td>
<td>195 ±15</td>
<td>431 ±65</td>
<td>86 ±5</td>
<td>301 ±49</td>
<td>15.1 ±3.5</td>
<td>0.29 ±0.06</td>
<td></td>
<td></td>
</tr>
<tr>
<td>GRE-0.5PVPA 1*,2*,3T*</td>
<td>540 ±40</td>
<td>60</td>
<td>18</td>
<td>330</td>
<td>4.2</td>
<td>0.05</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Note: * indicates that the sample did not ignite; Samples denoted as T represent in which thermocouples were inserted; FIGRA is fire growth rate index, defined as the ratio of PHRR and the time at which PHRR occurs.

![Figure 7.6: Mass loss versus time curves of the control and coated samples at 35 and 50 kW/m² heat fluxes without an ignition source](image)
Table 7.3: Digital images of residual char obtained at the end of cone calorimeter experiments of the control and coated GRE composite samples

<table>
<thead>
<tr>
<th>Heat flux (kW/m²)</th>
<th>Sample</th>
<th>Char residual images</th>
<th>Exposure time (s)</th>
<th>Char thickness (mm)</th>
<th>Expansion ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>35</td>
<td>Control</td>
<td>[Image]</td>
<td>450</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>GRE-0.3PVPA*</td>
<td>[Image]</td>
<td>450</td>
<td>28.7 ± 1.2</td>
<td>96 ± 4</td>
</tr>
<tr>
<td></td>
<td>GRE-0.5PVPA*</td>
<td>[Image]</td>
<td>450</td>
<td>32.0 ± 1.6</td>
<td>64 ± 3</td>
</tr>
<tr>
<td>50</td>
<td>Control</td>
<td>[Image]</td>
<td>400</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>GRE-0.3PVPA*</td>
<td>[Image]</td>
<td>400</td>
<td>29.3 ± 1.7</td>
<td>98 ± 6</td>
</tr>
<tr>
<td></td>
<td>GRE-0.5PVPA*</td>
<td>[Image]</td>
<td>400</td>
<td>37.3 ± 2.9</td>
<td>75 ± 6</td>
</tr>
</tbody>
</table>

Note: * indicates that the sample did not ignite; Expansion ratio is the char thickness divided by original coating thickness

The excellent thermal barrier and flame retardant properties of the GRE composites imparted from this PVPA coating could be attributed to the high concentration of phosphorus and nitrogen elements in its composition, and the coating working in a similar manner as an intumescent coating. The PVPA coating consists of three key components similar to that used in intumescent coatings which are the carbonisation agent, an acid source and a blowing agent [8]. On exposure to heat, the decomposition of the poly (vinyl phosphonic acid) generates phosphoric acid and water vapours. Similar to an intumescent system, the expandable charred layer of PVPA can be formed as the released acid could react with the carbon source, such as the polymer backbone of VPA (-CH₂-), to form a viscous fluid char layer, while the liberated water vapour acts as the blowing agent [8,9].
This charred layer provides a physical thermal barrier effect to delay ignition and further combustion of the underlying composite by impeding heat transfer and thus preventing the release of further flammable volatiles (pyrolysis products). In addition, this PVPA coating system also contains nitrogen in its tri-functional crosslinking agent (triallyl isocyanurate), which can synergistically increase the flame retardant action of the phosphorus-containing compounds [10,11].

When the heat flux was increased to 50 kW/m$^2$, the control sample showed an intense single peak the HRR curve similar to that observed at 35 kW/m$^2$ heat flux (see Figure 7.5 (c - d)), but the value of PHRR increases to 572 kW/m$^2$, whereas TTI and $T_{PHRR}$ decreases to 60 and 99 s, respectively. This results in an increase in FIGRA values of control sample (5.91 kW/m$^2$s). The THR value of the control sample also increases with increasing heat flux as expected (see Table 7.2).

For the PVPA coated samples, the HRR curves of GRE-0.3PVPA samples with ~320 µm coating thickness (GRE-0.3PVPA1 and GRE-0.3PVPA3 samples) are significantly different from the control sample, showing peaks of very low intensity to that of the control sample as can be seen from Figure 7.5 (c). The TTI was 195 s, after prolonged exposure to heat, the insulating effect of PVPA protective char layer is clearly seen from a very low heat release rate. With respect to the control sample, the TTI and $T_{PHRR}$ of GRE-0.3PVPA1 and GRE-0.3PVPA3 samples considerably increased to 195 and 301 s respectively, while the PHRR significantly decreased from 572 to 86 kW/m$^2$ and FIGRA decreased by 95 %. The THR values of those two GRE-0.3PVPA samples are also significantly lower than that of the control sample (see Table 7.2). On the other hand, all three replicate specimens of the PVPA-coated samples of 540 µm thickness (GRE-0.5PVPA) did not ignite, and showed lower PHRR, THR and FIGRA values than the GRE-0.3PVPA samples. Besides, a significant reduction in the mass loss rate was also observed for all PVPA-coated samples at 50 kW/m$^2$ heat flux. GRE-0.5PVPA sample showed a lower mass loss rate than the GRE-0.3PVPA sample as seen in Figure 7.6 (b). These observations are consistent with the char expansion results in Table 7.3. The char from GRE-0.5PVPA sample had the highest thickness (37.3 mm) followed by GRE-0.3PVPA (29.3 mm). This indicates that the thicker coatings provided a thicker char layer.
which is a better insulator and can prevent a rapid increase in the temperature during continued high radiant heat exposure.

From the cone results at 35 and 50 kW/m² heat fluxes, it can be concluded that the thermal barrier efficiency of the PVPA coating is strongly dependent upon the thickness of coating. Therefore, the optimum thickness providing the best thermal barrier/insulative performance to protect the GRE composite substrate lies in between 360 and 570 µm.

### 7.5 Thermal barrier effect of the PVPA chemical coatings

The temperature profile at the surface ($T_S$) and the back surface (unexposed) ($T_B$) of each sample was recorded during the cone experiments at 35 and 50 kW/m² heat fluxes, in order to evaluate the thermal barrier effect of PVPA coatings (in Section 3.7.3, Chapter 3). The temperature at the back surface ($T_B$) of all GRE samples as a function of time at both heat fluxes are plotted in Figure 7.7, and the times to reach 180 and 250 °C from temperature profiles at surface ($T_S$) and back surface ($T_B$) of all samples are reported in Table 7.4.

![Graphs showing temperature as a function of time for control and coated samples at 35 and 50 kW/m² heat fluxes without an ignition source.](image)

**Figure 7.7**: The back surface temperature ($T_B$) as a function of time for the control and coated samples at 35 and 50 kW/m² heat fluxes without an ignition source.
At 35 kW/m², the results in Figure 7.7 (a) show that although both PVPA-coated samples had a significant delay in temperature rise at the back surface after the sample was exposed to the heat compared to the control sample, the effect was more pronounced in GRE-0.5PVPA. At 50 kW/m², significant delays in temperature rise of the coated samples are also observed.

Table 7.4: The time required to reach the selected temperatures at the surface and back surface of all samples at different heat fluxes

<table>
<thead>
<tr>
<th>Heat fluxes (kW/m²)</th>
<th>Sample</th>
<th>Time (s) to reach 180 °C</th>
<th>Time (s) to reach 250 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Surface</td>
<td>Back surface</td>
</tr>
<tr>
<td>35</td>
<td>Control</td>
<td>19</td>
<td>55</td>
</tr>
<tr>
<td></td>
<td>GRE-0.3PVPA*</td>
<td>22</td>
<td>82</td>
</tr>
<tr>
<td></td>
<td>GRE-0.5PVPA*</td>
<td>23</td>
<td>92</td>
</tr>
<tr>
<td>50</td>
<td>Control</td>
<td>28</td>
<td>45</td>
</tr>
<tr>
<td></td>
<td>GRE-0.3PVPA*</td>
<td>32</td>
<td>75</td>
</tr>
<tr>
<td></td>
<td>GRE-0.5PVPA*</td>
<td>32</td>
<td>88</td>
</tr>
</tbody>
</table>

Note: * indicates that the sample did not ignite; only one sample was tested; The data in brackets, [], represent the increase (+) in time to reach a selected point of temperature for surface coated GRE laminates relative to the control sample.

The slower rise in temperature at those heat fluxes can be clearly seen by the increase in time to reach the softening temperature, 180 °C and pyrolysis temperature, 250 °C of the epoxy resin in Table 7.4. It can be seen that at 35 kW/m², the back surface temperature of the control sample reaches 180 and 250 °C within 58 and 86 s respectively, whereas the time to reach 180 and 250 °C in GRE-0.3PVPA sample are increased by 27 and 33 s. The further increase in time to reach both temperatures is observed in the thicker coating, i.e. in GRE-0.5PVPA sample time to reach 180 °C at back surface increased by 37 s and 250 °C by 80 s, compared to the control sample. A similar effect is also seen at 50 kW/m² heat flux in both GRE-0.3PVPA and GRE-0.5PVPA samples, the latter being more effective.
7.6 Effect of the coatings on the mechanical properties of the composites

The mechanical properties of the GRE laminates with/without PVPA coatings were studied in terms of impact and flexural moduli, using a drop weight impact and flexural three point bending tests (Section 3.8, Chapter 3).

7.6.1 Impact properties

The effect of PVPA-polymerised coatings on the impact modulus of the GRE laminate was studied using the impact drop-weight test at 5 J impact energy condition (4.62 kg drop weight with 110 mm drop height). The closed envelope load - deflection curves were obtained for all samples, as shown in Figure 7.8.

The load - deflection curves in Figure 7.8 imply the impactor would be pushed back after hitting the specimen due to a vibration effect, resulting in the rebound of loading (as discussed in Section 6.3.5.1, Chapter 6). The impact modulus of each sample was calculated from its initial load - deflection curve before the rebound (see Section 3.8, Chapter 3). In order to eliminate the effect of the difference of resin content in the laminates, the impact moduli for all the samples were normalised to 50% volume fraction of the glass fibre. Both of the impact modulus values before and after normalisation are reported in Table 7.5.
Table 7.5: The impact moduli calculated for all GRE composite laminates at 5 J energy level impact test

<table>
<thead>
<tr>
<th>Sample</th>
<th>Glass fibre content</th>
<th>Coating thickness</th>
<th>Impact modulus</th>
<th>Normalised impact modulus**</th>
<th>Change in modulus (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mass (wt%)</td>
<td>Volume fraction (vol%)</td>
<td>(µm)</td>
<td>(GPa)</td>
<td>(GPa)</td>
</tr>
<tr>
<td>Control</td>
<td>58</td>
<td>39</td>
<td>-</td>
<td>12.6 ±0.4</td>
<td>16.0 ±0.3</td>
</tr>
<tr>
<td>GRE-0.3PVPA</td>
<td>65</td>
<td>46</td>
<td>320</td>
<td>12.5 ±0.1</td>
<td>13.4 ±0.1</td>
</tr>
<tr>
<td>GRE-0.5PVPA</td>
<td>66</td>
<td>48</td>
<td>570</td>
<td>9.3 ±0.1</td>
<td>9.8 ±0.1</td>
</tr>
</tbody>
</table>

Note: % Change in modulus, (-) indicates reduction and (+) increase w.r.t respective value for the control; ** indicates the measured impact modulus value normalised to 50% volume fraction of the glass fibre; For glass fibre volume fraction calculation, glass fibre density = 2.5 g/cm³, epoxy matrix density at 25 °C = 1.17 g/cm³

From Table 7.5, the normalised impact modulus values of all samples show that the presence of 320 µm coating of PVPA reduced the modulus of the laminate by 16 % compared to the control sample. On increasing the coating thickness to 570 µm, the reduction of the impact modulus was more pronounced, i.e. 39 % lower than that of the control sample. This indicates that the thin coating (~ 300 µm) of PVPA coating had less effect on the impact modulus of the GRE laminate than the thicker coating.

7.6.2 The effect of impact on the physical properties of the coatings

The effect of impact on the morphology of this surface coating was studied. From the digital images of surfaces of post-impact samples shown in Table 7.6, from which damaged areas were also calculated both with 320 and 510 µm of PVPA coatings, there was no surface damage observed with both the 1 and 5 J impact conditions, which indicates that a PVPA coating show resilience under these conditions.
Table 7.6: Images of impact damage and damage observations on the front (impacted side) surfaces of all GRE specimens after 1 J and 5 J drop-weight impact tests

<table>
<thead>
<tr>
<th>Sample</th>
<th>Top-View images at surface</th>
<th>Damage observation</th>
<th>Damaged area (mm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>1 J</td>
<td>5 J</td>
</tr>
<tr>
<td>GRE-0.3PVPA</td>
<td><img src="image1" alt="Image" /></td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>GRE-0.5PVPA</td>
<td><img src="image2" alt="Image" /></td>
<td>X</td>
<td>X</td>
</tr>
</tbody>
</table>

Note: X: no damage appears, V: visible surface damage (The coating is damaged by the impact tup at a local area), D: debonding of coating and C: cracking of coating

7.6.3 Flexural properties

The effect of PVPA coatings on the flexural properties of the GRE laminates was studied by the three point bending test as discussed in Section 3.8.3 (Chapter 3). The load-extension curves obtained from three point bending test of all samples are shown in Figure 7.9, and their modulus results are given in Table 7.7.

![Figure 7.9: Load versus extension curves of the control and coated samples at room temperature from three point bending tests](image3)
Table 7.7: The flexural moduli of the control and coated GRE laminates

<table>
<thead>
<tr>
<th>Sample</th>
<th>Glass fibre content</th>
<th>Coating thickness</th>
<th>Flexural modulus</th>
<th>Normalised flexural modulus **</th>
<th>Change in modulus (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mass (wt%)</td>
<td>Volume fraction (vol%)</td>
<td>(µm)</td>
<td>(GPa)</td>
<td>(GPa)</td>
</tr>
<tr>
<td>Control</td>
<td>62</td>
<td>43</td>
<td>-</td>
<td>14.1 ±0.7</td>
<td>16.3 ±0.6</td>
</tr>
<tr>
<td>GRE-0.3PVPA</td>
<td>68</td>
<td>50</td>
<td>310 ±40</td>
<td>12.3 ±0.6</td>
<td>12.3 ±0.4</td>
</tr>
<tr>
<td>GRE-0.5PVPA</td>
<td>66</td>
<td>48</td>
<td>470 ±20</td>
<td>11.4 ±0.4</td>
<td>12.0 ±0.3</td>
</tr>
</tbody>
</table>

Note: % Change in modulus, (-) indicates reduction and (+) increase w.r.t respective value for the control; ** indicates the measured impact modulus value normalised to 50% volume fraction of the glass fibre.

The flexural modulus for all the samples in Table 7.7 were normalised to the 50% fibre volume fraction similar to that used in Section 7.6.1, and the values are given in Table 7.7. The results show that the normalised flexural moduli of coated samples are lower than the control sample. The presence of 310 µm PVPA coating (GRE-0.3PVPA) reduces the flexural modulus of the GRE laminates by 24 % compared to the control sample. This contributes to the fact that the flexural modulus PVPA film being less than the epoxy resin matrix in the GRE laminate. Therefore, the overall flexural modulus of coated sample is reduced [12]. With increasing thickness to 470 µm in GRE-0.5PVPA sample, the decrease in the flexural modulus was more pronounced as expected (26 % reduction with respect to the control laminate).

### 7.7 Flexural performance after exposure to different heat flux conditions

In this section, the flexural performance of the GRE composites with/without PVPA coatings after exposure to the radiant heat at different heat fluxes was investigated. All samples were exposed to a cone heater at 25 and 50 kW/m² heat fluxes for different exposure times. The residual flexural modulus of the samples was then measured by the three point-bending tests similarly to that of the samples in the previous section (see Section 3.8.3, Chapter 3).
Table 7.8: The flexural modulus and % modulus retention of the control and all coated samples after exposure to radiant heat of 25 and 50 kW/m² heat fluxes for different times

<table>
<thead>
<tr>
<th>Sample</th>
<th>Post-Exposure to 25 kW/m²</th>
<th>Post-Exposure to 50 kW/m²</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>120 s</td>
<td>240 s</td>
</tr>
<tr>
<td>Control</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Modulus ($E_f$)</td>
<td>% $E_f$ retention</td>
<td>Modulus ($E_f$)</td>
</tr>
<tr>
<td>Control</td>
<td>7.1 ±2.4</td>
<td>47 ±11</td>
</tr>
<tr>
<td>GRE-0.3PVPA</td>
<td>9.4 ±0.4</td>
<td>86 ±1</td>
</tr>
<tr>
<td>GRE-0.5PVPA</td>
<td>11.1 ±0.1</td>
<td>89 ±1</td>
</tr>
</tbody>
</table>

Figure 7.10: Digital images (side-view) showing damaged area after three point bending tests of the control and coated sample exposed to 25 and 50 kW/m² heat fluxes
The load was applied on the heat-exposed surface so that this particular surface would bear the compressive strain while the unexposed surface would be loaded in tension. In calculating the residual flexural modulus, due to the expansion of the PVPA coating during exposure to a cone heater, the final thicknesses after scrapping off the intumescent char from the test specimen were considered, and compared against that obtained at room temperature prior to heat exposure. The flexural modulus and percentage retention of this measure for all post-heat exposure samples are reported in Table 7.8. Digital images for all post-heat exposure samples after the three point-bending test are presented in Figure 7.10. The results show that the control laminate after exposure to 25 kW/m² for 120 s showed 47 % flexural modulus retention, while both PVPA coated samples had > 86% retention. GRE-0.3PVPA sample retained 86 % of the original flexural modulus. As can be clearly seen from digital images in Figure 7.10, the control laminate showed significant loss in the structural integrity after exposure to 25 kW/m² heat flux for 120 s, where delamination can be observed between glass fibres and resin matrix, especially at top surface. On the other hand, GRE-0.3PVPA and GRE-0.5 PVPA samples did not show any delamination. The structural integrity of the laminate was retained in both PVPA coated samples. As the exposure time was increased to 240 s, the control laminate lost most of flexural strength, only 13 % modulus was retained. Whereas, both PVPA coated samples could retain > 50% flexural property of GRE composite, i.e. GRE-0.3PVPA retained 66 % and GRE-0.5PVPA retained 84 % of the original flexural modulus of its control laminate (Table 7.8). This observation is consistent with the results after 240 s exposure to 25 kW/m² in Figure 7.10, where the complete loss in structural integrity of the GRE composite laminate without PVPA coatings, i.e. the glass fibres torn apart from composite structure can be seen. With PVPA coatings, both GRE-0.3PVPA and GRE-0.5PVPA samples showed some degree of delamination, but not to the same extent as in the control sample.

When the heat flux was increased to 50 kW/m² and exposure time was reduced to 30 s, the control sample retained 73% of its original flexural modulus, while GRE-0.3PVPA and GRE-0.5PVPA samples retain 88 and 93% of their original flexural moduli, respectively. This can be correlated with the results in Figure 7.10, which show that the control sample displayed a degree of heat damage in the composite structure of the
sample, but PVPA coated samples did not show any damage to the structure. These results indicate that the PVPA coatings could promote efficient thermal barrier protection to the GRE composites at higher heat fluxes.

7.8 Durability of coatings

7.8.1 Effect of water on PVPA chemical coatings

7.8.1.1 Wettability

The wettability of the PVPA coated surfaces was studied by the water drop test (see Section 3.6.3 (Chapter 3)). The images of a water droplet on a sample surface at 0, 1, 60 and 120 s are shown in Figure 7.11.

![Figure 7.11: Surface wettability of different PVPA coated GRE laminates at various times](image)

The results in Figure 7.11 show that after a drop of water is placed on the control laminate surface, the water droplet on the surface continually retains its droplet shape for 120 s, indicating the hydrophobic nature of the GRE surface. For the GRE-PVPA sample, the water drop remains as a droplet on the PVPA coated surface until 60 s, but then the water droplet becomes flatter at 120 s. This indicates that the application of a PVPA coating increases the wettability and hydrophilicity of the GRE composite surface.
7.8.1.2 Durability of the coating after immersion in water

The durability of the PVPA coatings to water was studied using the water-soak test.

Table 7.9: The digital images of all GRE surfaces before and after the water-soak test and weight loss (wt%) after the test

<table>
<thead>
<tr>
<th>Sample</th>
<th>Images</th>
<th>% Weight loss after 24 h soaking in water and 24 h drying at RT</th>
<th>% Weight loss after drying at 100°C for 2h</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>-</td>
<td>-0.03 ±0.01</td>
<td>-0.10 ±0.07</td>
</tr>
<tr>
<td>GRE-0.3PVPA</td>
<td><img src="image1.png" alt="Image" /></td>
<td>-67.2 ±3.5</td>
<td>-69.2 ±3.6</td>
</tr>
<tr>
<td>GRE-0.5PVPA</td>
<td><img src="image2.png" alt="Image" /></td>
<td>-75.3 ±2.6</td>
<td>-77.2 ±2.6</td>
</tr>
</tbody>
</table>

The effect of water on the durability of this coating is reported in Table 7.9 in terms of the weight change after the water soaking and changes in the surface morphology, observed by digital images of the surfaces. The digital image of the GRE-0.3PVPA sample in Table 7.9 clearly shows a significant removal of the coating from the surface of the GRE laminate after 24 h soaking in water, quantified as 67.2 wt% weight loss. A further weight loss of 69.2% was observed after drying in an oven at 100 °C. Similarly, the sample with the thicker coating, (GRE-0.5PVPA), showed a 75.3% weight loss after water soak test and drying at room temperature, increasing further to 77.2% after drying at 100 °C. These results indicate that the PVPA coating is hygroscopic. This is likely due to a large number of hydroxyl groups in the vinyl phosphonic acid (VPA) polymer, which cause a very high hydrophilic character to the coating.
7.8.2 Adhesion between coatings and GRE surfaces

The adhesion between two different thicknesses of PVPA coatings and GRE composite surfaces was studied using the tape pull test.

Table 7.10: The changes in weight after the tape pull test from different areas of the coated samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Thickness of coating (µm) and coating deposition (wt%)</th>
<th>Images of the tapes after tape pull test</th>
<th>Total weight loss (%)</th>
<th>% Peeling of the coating</th>
</tr>
</thead>
<tbody>
<tr>
<td>GRE-0.3PVPA</td>
<td>320, 14.4%</td>
<td></td>
<td>0.01±0.01</td>
<td>-</td>
</tr>
<tr>
<td>GRE-0.5PVPA</td>
<td>510, 21.1%</td>
<td></td>
<td>0.00 ±0.02</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 7.10 shows the loss in weight and % coating peeled off after the tape test at 180° pulling angle for all the coated samples. Digital images of all the tapes after each test were taken and are also shown in Table 7.10. The images of the tapes and their weight loss after peeling show that there was no observed peeling of the PVPA coating in both coated samples. This indicates that during polymerisation the VPA monomers, there is chemical bonding with the epoxy resin on the GRE surface resulting in a high adhesion strength at the interface between coating and substrate.

7.9 Conclusions

A vinyl phosphonic acid polymer (PVPA) coating can be uniformly polymerised on the GRE composite surface via UV photo-polymerisation. The PVPA thin film was chemically bonded to the epoxy surface and the coating did not peel off when subjected to the tape pull test. However, after 24 h of ageing in water, the PVPA coated samples showed the removal of coating and a significant weight change, which indicates the very poor water resistance of the coating.
In terms of thermal barrier properties, the PVPA coating prevented ignition at 35 kW/m² and delayed TTI at 50 kW/m². There was a significant reduction in PHRR, THR and FIGRA values compared to those of the GRE composite. This PVPA coating could also delay and reduce the heat transfer through the laminate. The thermal barrier effect of this PVPA coating increased with increasing coating thickness. The best results were observed with an ~500 µm thick coating.

In terms of mechanical properties, although the PVPA coating decreased the impact and flexural muduli of the GRE composite, the reduction (< 30%) is not significant. The increase in coating thicknesses further reduced the impact and flexural moduli. However, the PVPA coatings can maintain the flexural strength of the GRE composite up to 240 s after exposure to 25 kW/m² heat flux and for 30 s at 50 kW/m² heat flux. Moreover, the PVPA coatings were resistant to cracking / debonding after the 5 J energy impact drop weight test.

Finally, it is worth pointing out that although the polymerisation of vinyl phosphonic acid monomers provided a very efficient thermal barrier protection to the GRE composite without significantly affecting its physical and mechanical properties, the durability to water is very low, which should be the focus of any future study.

7.10 References


Chapter 8

CONCLUSIONS

The main aim of this research was to develop novel thermal barrier surface coatings to improve the fire retardant properties of glass fibre-reinforced epoxy (GRE) composites, without affecting the physical and mechanical properties of the composite substrate. A number of different types of materials and surface coating techniques have been used to develop four types of coatings; namely intumescent coatings (Chapter 4), nanoclay/particles depositions (Chapter 5), ceramic particles containing coatings (Chapter 6) and a chemical coating polymerised on the surface of the laminate (Chapter 7). The experimental work involved the application of the surface coatings on GRE composite laminates (pre-prepared) by paint brushing on commercial intumescent coatings; spraying nanoclays dispersed in a solvent on plasma activated GRE laminate surfaces; applying nano/micro ceramic particles dispersed in a resin by painting or K-bar application; and applying a chemical coating via polymerisation of phosphorus-containing monomers using UV radiation. The main conclusions drawn from their flammability and mechanical tests results are presented in the following section.

8.1 Conclusions

Intumescent coatings: Commercial intumescent coatings M90, M93 and FX5002 (Leighs’ Paints, UK) of 1, 3 and 5 mm thickness were applied on GRE laminate surfaces (Chapter 4). When tested with a cone calorimeter at 50 kW/m² heat flux, the coatings had no effect on TTI, but significantly reduced the PHRR by > 50 % compared to the control sample. Coated samples burnt slowly, but for a longer time, resulting in an increase in THR values. The coating also delayed the heat transfer through the laminate,
measured by time to reach surface temperature of the laminate (below the coating) at 180 °C (softening temperature of the epoxy resin). Temperature dependent thermal conductivity measurements of the intumescent coatings showed a good co-relation with char expansion, and it was observed that ~ 0.2 W/mK is the minimum thermal conductivity value of ~ 3 mm thick char that should be able to protect a composite structure from heat to maintain structural integrity for a period of time.

**Nanoclay coatings:** Cloisite 30B nanoclay was applied onto the GRE composite surface by two different methods. In one method, the nanoclays were deposited to the surface previously activated by an atmospheric argon plasma (Ar-plasma) with or without the incorporation of a silicon-containing monomer (HMDSO), and then further treated with the Ar-plasma again. Alternatively, the coating was applied using a phenolic resin binder. From the results in **Chapter 5**, it could be concluded that the nanoclay particles were uniformly deposited onto the GRE composite surface after argon plasma treatment or with the resin binder and the coating did not peel off when tested by the tape pull test. With Ar-HMDSO plasma, however, the adhesion between the nanoclays and the laminate surface was slightly less than that from Ar-plasma. At a 35 kW/m² heat flux in the absence of an ignition source, the concentration of nanoclays on the surfaces in all three nanoclay coatings was too low (3-4 wt% deposition) to show any significant improvement in flame retardant and thermal barrier properties.

**Ceramic particle coatings:** The effectiveness of the application of ceramic nano/micro particle coatings on GRE composites was considered in **Chapter 6**. Initially, the coating was prepared using the Ceepree, Recoxit and zirconia particles with a DOPO-flame-retarded epoxy resin binder. At 20 to 50 kW/m² heat fluxes in the presence of an ignition source, the thermal barrier protection by these coatings could reduce the burning behaviour of GRE composites by decreasing PHRR and increasing T\_PHRR values. However, the effect of DOPO-flame-retarded, epoxy binder and the resin-rich surface caused a reduction in TTI values of the GRE composites. These initial results suggested that the ceramic particles in the coatings act only as thermal insulators, but they are not flame retardant. The flame retardancy of the resin binder should be improved in order to...
delay/stop ignition of the underlying composite. Another important conclusion was that for a better thermal barrier performance, the ceramic particles should completely cover the surface. It was, therefore, decided to use an inherently flame retardant phenolic resin for dispersing and depositing nanoclay, nanosilica, Flekashield, Recoxit and zirconia particles using a K-bar coater on the GRE composite surfaces. Approximately 100-500 µm thick coatings with 1-14 wt% particle deposition, depending upon the nature of the ceramic particles were obtained. In another set, the particle concentration on the surface was increased by sieving the dry particles onto the wet surface coating. At 35 and 50 kW/m² heat fluxes in the absence of an ignition source, all the coatings were very effective in increasing TTI, reducing PHRR and delaying T_PHRR of the GRE composite. All ceramic particle coatings were durable to tape pull and water-soak tests. Almost all ceramic coatings decreased the impact and flexural moduli of the GRE composite, the reduction depended upon the particle size and thickness of the coating. Surface fractures were observed in all the coated samples after impact drop weight testing, but all the coated GRE composites showed a higher flexural property retention than un-coated GRE composite after exposure to 25 kW/m² for 120 s and 50 kW/m² for 30 s.

Chemical coating: The VPA monomer was mixed with 5 wt% of the photo-initiator (Darocur1173) and 5 wt% of the crosslinking agent (triallyl isocynurate) and applied onto GRE laminate surfaces to give liquid films of approximately 300 and 500 µm thicknesses. After UV irradiation in an in-house UV chamber for 5-6 h, a uniform poly (vinyl phosphonic acid) (PVPA) film on the laminate was obtained. The results of chemical coating by VPA polymerisation in Chapter 7 showed that the polymerisation of the VPA monomer proceeds via a UV radical mechanism during exposure to the UV radiation. At 35 kW/m² heat flux in the absence of an ignition source, the PVPA films formed an expanded char acting as a very effective thermal barrier protection, which caused the non-ignition in all the coated samples, while a 540 µm thick coating was required to achieve non-ignition at 50 kW/m². The PVPA films also had the potential to reduce the heat transfer in GRE composite. The thermal barrier performances of PVPA films strongly depended upon thickness of the films. Apart from expanded char formation, the superior thermal barrier properties of the PVPA films could be also
attributed to the presence of nitrogen from the triallyl isocynurate crosslinking agent that cause synergistic enhancement in the efficiency of phosphorus-contained monomer. In terms of durability, the PVPA films could resist cracking and peeling after the impact drop weigh test and did not peel off when subjected to the tape pull test. However, the PVPA films are very sensitive to water due to the hydroxyl group in VPA monomer. After 24 h of ageing in water, the results showed a significant removal of coating and potential weight loss.

8.2 Comparison of the performances of the four types of coatings

In the beginning of this PhD work, the thermal barrier effect of three intumescent coatings on glass fibre-reinforced epoxy composites was studied (Chapter 4) with a view of setting a benchmark to evaluate the performance of other coatings to be developed. Based on the results, the target performance of an ideal coating during exposure to 50 kW/m² in a cone calorimeter was set as; it should not ignite or should increase TTI, reduce PHRR ≥ 50% compared to uncoated composite and should not prolong burning time. Moreover, the coating should delay the time-to-reach a surface temperature equal to softening temperature of the resin (180 °C) by more than 50%. However, during the course of the work it was realised that some of the coatings being developed were too thin compared to the expanded chars of the intumescent coatings, to achieve that target performance. In order to fully evaluate their thermal barrier efficiency, those coated samples were tested at < 50 kW/m² and without spark ignition. To compare their results, a new set of criteria as given in Table 8.1 has been set. The comparison of flammability and thermal barrier properties are summarised in Table 8.2, while the mechanical properties and the durability are compared in in Table 8.3.
Table 8.1: Criteria set for comparison of different coatings

<table>
<thead>
<tr>
<th>Mark</th>
<th>Flammability and thermal barrier properties</th>
<th>Durability</th>
<th>Mechanical properties</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Delay in TTI</td>
<td>% Reduction in PHRR</td>
<td>Delay in TPHRR</td>
</tr>
<tr>
<td>-</td>
<td>&lt; 10 s</td>
<td>&lt; 10</td>
<td>&lt; 10 s</td>
</tr>
<tr>
<td>+</td>
<td>10-50 s</td>
<td>10-30</td>
<td>10-50 s</td>
</tr>
<tr>
<td>++</td>
<td>50-100 s</td>
<td>30-50</td>
<td>50-100 s</td>
</tr>
<tr>
<td>+++</td>
<td>100-200 s</td>
<td>50-70</td>
<td>100-200 s</td>
</tr>
<tr>
<td>++++</td>
<td>No ignition</td>
<td>70-90</td>
<td>&gt; 200 s</td>
</tr>
</tbody>
</table>

Note: - indicates unclassified results
*180 °C was chosen as it is the glass transition temperature of the epoxy resin in GRE composite
** indicates % retention of flexural modulus after exposure to 25 kW/m² for 120 s

From Table 8.2 the efficiency of different coatings in terms of fire retardancy and thermal barrier performances with regard to intumescent coatings can be ranked as:

In term of fire retardancy (delay in TTI, decrease in PHRR and increase in TPHRR):

Chemical coatings > Ceramic particle coatings > Nanoclay deposition

In term of thermal barrier effect:

Chemical coatings > Ceramic particle coatings >> Nanoclay deposition

The thermal barrier efficiency of a coating depends upon the formation of a uniform thermally insulative layer on the surface of the burning polymer, where the protective layer needs to be thick enough in order to insulate the underlying polymer. The better performance of the chemical coating can be explained due to formation of an intumescent char, which acts as a thermal barrier. On the other hand, nanoparticles or micro-ceramic particles layers were not thick enough to provide a thermal barrier effect for an extended period of time.
Table 8.2: Comparison of flammability and thermal barrier properties at 35 and 50 kW/m² of the different types of coatings

<table>
<thead>
<tr>
<th>Type of coating</th>
<th>35 kW/m²</th>
<th>50 kW/m²</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Delay in TTI</td>
<td>Reduction in PHRR</td>
</tr>
<tr>
<td>Intumescent coatings (Ignition on)</td>
<td>M90 1 mm</td>
<td>NT</td>
</tr>
<tr>
<td></td>
<td>M93 1 mm</td>
<td></td>
</tr>
<tr>
<td></td>
<td>FX5002 1mm</td>
<td></td>
</tr>
<tr>
<td>Nanoclay depositions (Ignition off)</td>
<td>Ar-plasma</td>
<td>++</td>
</tr>
<tr>
<td></td>
<td>HMDSO/Ar-plasma</td>
<td>+</td>
</tr>
<tr>
<td></td>
<td>Phe- binder</td>
<td>++++</td>
</tr>
<tr>
<td>Ceramic particles coatings (Ignition off)</td>
<td>Nanoclay</td>
<td>++</td>
</tr>
<tr>
<td></td>
<td>Nanosilica</td>
<td>++++</td>
</tr>
<tr>
<td></td>
<td>Flekashield</td>
<td>++++</td>
</tr>
<tr>
<td></td>
<td>Recoxit</td>
<td>++</td>
</tr>
<tr>
<td></td>
<td>Zirconia</td>
<td>++</td>
</tr>
<tr>
<td></td>
<td>Flekashield**</td>
<td>++++</td>
</tr>
<tr>
<td></td>
<td>Recoxit**</td>
<td>++</td>
</tr>
<tr>
<td></td>
<td>Zirconia**</td>
<td>++</td>
</tr>
<tr>
<td>Chemical coatings (Ignition off)</td>
<td>300 µm thick film</td>
<td>++++</td>
</tr>
<tr>
<td></td>
<td>500 µm thick film</td>
<td>++++</td>
</tr>
</tbody>
</table>

Note: * The temperature at back surface (un-exposed) of the sample
** indicates addition of ceramic particles on the coating surfaces
NT = not tested
Table 8.3: Comparison of durability and mechanical properties of the nanoclay depositions, ceramic particle coatings using a phenolic resin as binder and chemical coatings

<table>
<thead>
<tr>
<th>Type of coating</th>
<th>Durability</th>
<th>Effect of coating on mechanical properties</th>
<th>% Modulus retention after exposure to 25 kW/m² for 120 s</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Peeling</td>
<td>Water</td>
<td>Resistance to 5J impact energy*</td>
</tr>
<tr>
<td>Nanoclay</td>
<td>++++</td>
<td>++</td>
<td>NT</td>
</tr>
<tr>
<td>Ar-plasma</td>
<td>+</td>
<td>-</td>
<td>NT</td>
</tr>
<tr>
<td>HMDSO/Ar-plasma</td>
<td>+</td>
<td>+++++</td>
<td>NT</td>
</tr>
<tr>
<td>Phe-binder</td>
<td>+++++</td>
<td>++++</td>
<td>NT</td>
</tr>
<tr>
<td>Nanoclay</td>
<td>++++</td>
<td>++++</td>
<td>✓</td>
</tr>
<tr>
<td>Nanosilica</td>
<td>++++</td>
<td>++++</td>
<td>✓</td>
</tr>
<tr>
<td>Flekashield</td>
<td>++++</td>
<td>++++</td>
<td>✓</td>
</tr>
<tr>
<td>Recoxit</td>
<td>++++</td>
<td>++++</td>
<td>✓</td>
</tr>
<tr>
<td>Zirconia</td>
<td>++++</td>
<td>++++</td>
<td>✓</td>
</tr>
<tr>
<td>Flekashield**</td>
<td>++++</td>
<td>++++</td>
<td>✓</td>
</tr>
<tr>
<td>Recoxit**</td>
<td>++++</td>
<td>++++</td>
<td>✓</td>
</tr>
<tr>
<td>Zirconia**</td>
<td>++++</td>
<td>++++</td>
<td>✓</td>
</tr>
<tr>
<td>Chemical</td>
<td>300 µm thick film</td>
<td>++++</td>
<td>-</td>
</tr>
<tr>
<td>coatings</td>
<td>500 µm thick film</td>
<td>++++</td>
<td>-</td>
</tr>
</tbody>
</table>

Note: * The resistance to impact observed visually from the impacted specimens
  ✓ = no crack; ✓ = crack; NT = not tested
  ** indicates addition of ceramic particles on the coating surface
In Table 8.3, the effect of coatings on the mechanical properties and the durability of each coating are compared. The physical properties of these coatings can be ranked as:

**In term of adhesion:**

**Chemical coatings ≈ Ceramic particle coatings > Nanoclay deposition**

The results obtained showed that all the coating types containing a resin binder and the polymerisation of monomer film on the substrate have a higher durability performance with respect to peeling than all the coating without any binder.

**In terms of water resistance:**

**Ceramic particle coatings > Nanoclay deposition >> Chemical coatings**

The ceramic particle coating types containing resin binder showed the best performance. The durability to water of the coatings depends not only on its chemical bonding between the coating and substrate, but also on the nature of the coating material used. For instance, the resin binders such as phenolic resin are relatively hydrophobic, but the poly (vinyl phosphonic acid) is hydrophilic, which adsorbs water readily.

**In terms of resistance to impact:**

**Chemical coatings > Ceramic particle coatings**

The PVPA films have much higher resistance to cracking and debonding than the ceramic particle coatings after being subjected to an impact drop weight.

**In terms of effect on mechanical properties of laminate:**

**Chemical coatings > Ceramic particle coatings**

These results suggested that the presence of thin ceramic particle coatings had a minor effect in the reduction of impact and flexural properties of the GRE laminates, while thick ceramic particle and chemical coatings had significant effects on those properties.
In terms of retention of structural integrity after exposure to 25 kW/m$^2$ for 120 s:

**Chemical coatings > Ceramic particle coatings**

Both types of the coatings could significantly maintain the flexural property of the GRE composites after heat exposure to 25 kW/m$^2$ for 120 s.

## 8.3 Suggestions for future work

The purpose of this thesis was the development of surface coatings that could provide thermal barrier protection to glass fibre-reinforced epoxy composite substrates. Future work should focus on the application of nanoclays, ceramic particles and chemical coatings on alternative polymeric composite substrates, such as carbon fibre-reinforced epoxy composite, glass fibre-reinforced unsaturated polyester composites, etc., in order to collect more data on thermal barrier performance of these surface coatings. Another area of activity would be improvement in the technique of covering the surface with the ceramic particles and increasing particle concentrations, these play an important roles in the thermal barrier protection. The deposition of ceramic particle coatings could be obtained through high pressure spraying and layer-by-layer assembly techniques. The possibility of creating multi-layer coatings on surfaces could also be explored. Similarly, the nanoclay coatings could be further improved by using alternative deposition methods such the sol-gel technique.

Further study should investigate making PVPA coatings hydrophobic. The chemical functionalisation of VPA monomer should be explored in order to reduce a number of hydroxyl groups, which attribute a very high hydrophilic character to this coating. Alternatively, the possibility of depositing a very thin hydrophobic layer over PVPA film could be of interest.