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UV-polymerisable, phosphorus-containing, flame-retardant surface coatings for glass fibre-reinforced epoxy composites

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ABSTRACT

A vinyl phosphonic acid based flame retardant coating has been applied on the surface of a glass-fibre reinforced epoxy (GRE) composite substrate using a UV polymerisation technique. On exposure to heat the poly (vinyl phosphonic acid) (PVPA) coating thus obtained, intumesces and acts as a thermal insulator, providing active fire protection to the composite structure. Samples with ~300 and 500 μm thick coatings were prepared. The fire performance of the coated GRE composite was studied by cone calorimetry at 35 and 50 kW/m^2 heat fluxes. While the sample with ~500 μm thick coating did not ignite at both heat fluxes, the one with the ~300 μm thick coating ignited at 50 kW/m^2 , however the time-to-ignition was delayed from 60 s in the uncoated sample to 195 s and the peak heat release rate reduced from 572 kW/m^2 to 86 kW/m^2 . The coatings did not peel off when subjected to a tape pull test and resisted cracking/debonding during an impact drop test of up to 5 J energy. However, the coatings are hydrophilic, showing significant mass loss in a water soak test. The improvement of the hydrophobicity of these coatings is a focus of our future research.

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1. Introduction

Flame retardant (FR) coatings have been used for centuries to protect different substrates ranging from textiles, wood, metals and recently organic polymers, against fire. The major advantage of surface coatings as opposed to adding flame retardants (FRs) in the bulk of material is that this method allows the concentration of FR chemicals on the surface of the substrate [1,2], which apart from effectively protecting the substrate from ignition helps in preserving the mechanical properties of the material [3,4]. Conventional flame retardant coatings either intumescent or non-intumescent types contain flame retardant chemicals dispersed in a binder and the formulation is then applied on the surface of the substrate [5–7]. The use of resin binder however, adds extra fuel, hence the FR chemicals have to be in relatively large proportions to be effective, making the coating thicker. To avoid the use of resin, flame retardant monomers can be directly polymerised on the surface of the substrate containing some functional groups. In recent years, phosphorus-containing monomers have gained significant development in FR coating applications, owing to the flame

retardant effect of these compounds. The phosphonate functionality in a monomer can promote char formation during combustion [8] and the char thus formed can provide a thermal barrier to the underlying substrates. The monomers containing phosphonate functionality (i.e. vinyl phosphonic acid (VPA), several dialkyl vinyl phosphonates, and various vinyl and allyl phosphine oxides) have been used as monomers for copolymerisation with one or two comonomers [6,9], or as oligomers that react with the polymer binder to form a branched or grafted phosphorylated polymer [10,11]. Furthermore, some of these phosphorus-containing monomers can be directly grafted or polymerised on textile substrates to obtain a phosphorylated polymer film [12,13], for instance, VPA monomer polymerised on finished textiles (i.e. cotton, polyamide, polyacrylonitrile and polyester), via photo-induced polymerisation [13]. The resulting coated textiles showed high levels of flame retardant performance and passed a vertical flammability test for protective clothing.

In this work, the synthesis, characterisation, and polymerisation of vinyl phosphonic acid monomer on a glass-fibre reinforced epoxy (GRE) composite substrate are reported. This is more challenging than the textile substrates, where the surface is easily wet and the chemical structures of the textiles have more reactive groups. In the case of GRE the outer surface is mainly cured epoxy resin with very few hydroxyl groups for reacting with the VPA monomer.

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2. Experimental

2.1. Materials

2.1.1. Glass fibre-reinforced epoxy (GRE) composite

Epoxy resin system: epoxy phenol novolac resin (Araldite LY5052, Huntsman) and cycloaliphatic polyamine-2,2-dimethyl-4,4-methylene bis cyclohexylamine hardener (Aradur HY 5052, Huntsman).

Glass fibre: woven roving glass fibre of E-glass type (300 g/m², Glasplies).

2.1.2. VPA surface coatings

- (i) Monomer (VPA): vinyl phosphonic acid, Rhodia UK Ltd.
- (ii) Crosslinking agent: triallyl isocyanurate, TAICROS® (TCI Europe N.V.)
- (iii) Photo-initiator: 2-hydroxy-2-methylpropiophenone, Darocur 1173 (TCI Europe N.V.)

2.2. Sample preparation

2.2.1. Glass fibre reinforced epoxy (GRE) composite

Eight pieces of 300 mm × 300 mm woven E-glass fabric were used for composite preparation, with the ratio of 50 wt% glass fibre and 50 wt% resin matrix. The GRE composite samples of ~3 mm thicknesses were fabricated using a hand lay-up method by impregnating each glass fabric layer with the resin using 30 wt% hardener w.r.t. resin, vacuum bagging and curing at room temperature (RT) for 24 h, and then post-curing at 80 °C for 6 h.

2.2.2. Polymerisation of VPA monomers on the GRE composite

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 × 150 mm) using a paint brush to obtain coatings of approximately 300 and 500 μm thicknesses. Following this the coated samples were irradiated for given times in a photoreactor consisting of six 15 W UV black light bulbs, which have a peak emission at 360 nm wavelength. Irradiation distance was 30 mm. In order to eliminate the scavenging effect of oxygen during photo-polymerisation, nitrogen gas (99.99% purity with flow rate of 10 l/min) was purged into the photoreactor at all time. After UV irradiation for 5 h (300 μm thick) and 6 h (500 μm thick), the VPA-coated GRE composite sample was removed from the photoreactor and then post-cured at 80 °C for 24 h in an oven.

2.3. Physical and morphological characterisation of coatings

All samples were weighed before and after the coating application and the wt% polymer coating deposited on the surface was calculated. The thicknesses of coatings were obtained from the difference of thicknesses of coated and uncoated samples, measured using a digital calliper.

The morphologies of poly (vinyl phosphonic acid), (PVPA) surface coatings were studied using scanning electron microscopy (SEM, Hitachi Technologies Model 3400) with accelerating voltage capacity 1–30 kV and magnification ranges between 10× and 300,000× at 30 kV providing resolution down to 10 μm. All samples were cut into 5 mm × 5 mm pieces and mounted on aluminium stubs with double sided conductive adhesive tapes. The metalization on the coated surfaces with gold was performed in argon atmosphere (20 Pa) using an Emitech SC7620 Mini Sputter Coater, with a current of 20 mA for 60 s.

The chemical composition of the PVPA surface coating was studied by infrared attenuated total reflection spectroscopy (IR-ATR). In this technique, the sampling depth can be up to ~1 μm. The surfaces of coated samples were scanned in the range of 4000–600 cm⁻¹ and recorded with a Nicolet iS10 spectrophotometer (Thermo Scientific). An IR spectrum also allows investigation of the polymerisation of the VPA monomer.

2.4. Flammability and thermal barrier study

The flammabilities of all GRE composites with and without VPA surface coating were evaluated using a cone calorimeter (Fire Testing technology, UK). Sample size used was 75 mm × 75 mm, three replicate tests were carried out and the results averaged. The size of specimens used in this study is smaller than the standard size as dictated by ISO 5660-1 owing to the limitation in the quantity of composite panels manufactured. However, previous work performed in our laboratory [14] revealed that the fire performance is geometry independent at least within the range of dimensions considered in this study. Moreover, the cone calorimeter data determined in the study are presented on a relative basis with respect to the control composite. All samples were tested by exposing them to 35 and 50 kW/m² heat fluxes in the horizontal mode at a distance of 25 mm from the cone heater without a spark ignition source. The different flammability parameters are reported as time-to-ignition (TTI), heat release rate (HRR), peak heat release rate (PHRR), time-to-PHRR (T_{PHRR}), total heat release (THR) and total smoke release (TSR).

In order to study the thermal barrier properties of each thickness of PVPA coating, three *K*-type thermocouples were placed, one on top of the surface coating and two on the back surfaces of samples. The thermocouples recorded temperature as a function of time using a recorder data logger for the duration of exposure to various heat fluxes during the cone experimental. Two specimens were tested and the average temperature–time profiles are reported in this study.

2.5. Flexural properties of heat/fire damaged samples

The effect of one-sided radiant heating on the residual flexural moduli, E_f , of GRE composite samples with and without surface coatings was investigated. Test specimens (125 mm × 13 mm × ~3 mm) were exposed to one-sided radiant heat fluxes of 35 and 50 kW/m² from a distance of 25 mm for varying periods (35 kW/m² for 120 and 240 s; 50 kW/m² for 30 s). The heat fluxes and exposure times were selected based on the cone results to ensure that the sample should not ignite. If the sample ignited, the flame was immediately quenched with a fire proof fabric followed by cooling in a ventilated room. The heat-damaged specimens were allowed to cool down naturally to ambient temperature before the residual char was scraped off. The flexural moduli of all test specimens were determined prior to coating and following fire exposure via a three-point bending test. For heat-damaged GRE composite samples, bending loads were applied on the heat-exposed surface of the test specimen using a 100 N load cell Instron 3369 tensometer in the displacement control mode (cross-head speed of 1 mm/min). The flexural moduli values were then calculated using the Engineers' bending equation [15]:

$$E_f = \frac{l^3}{4bh^3} K \quad (1)$$

where l is the test span, h the thickness, b the width of the specimen and K is the flexural stiffness (e.g., the slope of the load–displacement curve). Two independent measurements were performed on each composite sample with the average data presented.

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