



# A strategy and mechanism of fabricating flame retarding glass fiber fabric reinforced vinyl ester composites with simultaneously improved thermal stability, impact and interlaminar shear strengths



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## ABSTRACT

Poor flame retardancy, even worse than that of their matrix, is the common bottleneck for glass fiber (GF) reinforced polymeric composites (GFRPs), however, overcoming this problem generally degrades other performances of GFRPs. Herein, new GF fabric (PHSi-g-GF) grafted with phosphorus-containing hyperbranched polysiloxane (PHSi) through grafting-from technique, and new matrix (PSiVE) consisting of vinyl ester matrix (VE) and PHSi were prepared to develop new composites; meanwhile other three kinds of composites (GF/VE, PHSi-g-GF/VE, GF/PSiVE), of which at least one composition (matrix or fabric) is the original one, were also fabricated. The flame retardancy, thermal and mechanical performances of these composites were intensively studied and compared. Results show that PHSi-g-GF/VE and GF/PSiVE composites have much better integrated performances than GF/VE composite. Interestingly, the PHSi-g-GF/PSiVE composite has the best flame retardancy, for example, compared with GF/VE composite, PHSi-g-GF/PSiVE composite has 7 s longer time to ignition and 34% lower peak of heat release rate as well as 13% higher limited oxygen index and much higher UL-94 grade. This is originated from the unique dual flame retarding mechanisms in both gaseous and condensed phases. In addition, PHSi-g-GF/PSiVE composite has significantly improved thermal stability, 14% higher interlaminar shear and 60% higher impact strengths than GF/VE composite, completely overcoming the common problems of GFRPs. The presence of PHSi provides good interaction between GF and matrix as well as toughening effect on VE resin due to the flexible Si–O–Si chain and cavity structure of PHSi. These attractive improvements in the performances of PHSi-g-GF/PSiVE composite demonstrate that the method and mechanism provided herein are effective to develop high performance GFRPs.

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## 1. Introduction

As one important kind of polymer matrix composites, glass fiber (GF) reinforced polymer composites (GFRPs) have gained extensive attentions worldwide and gotten rapid development since the 1940s, and have been widely employed in almost all fields including aerospace [1], electronic information [2], new energy [3], medical instrument [4], architecture [5], transportation [6] and sports [7], etc. Higher performance and multi-functionalization have always been the development trends of GFRPs. In recent years, besides

higher thermal stability and mechanical properties, good flame retardancy has become one of key properties due to the harsh requirement on sustainable development.

In fact, poor flame retardancy has been the shortcoming of GFRPs. For the past years, this property was not included in the list of key properties of GFRPs, so it was not given enough attentions until recent years. As is well known, almost all polymers do not have good flame retardancy, however, the majority of GFRPs has been found to have even higher flammability than their matrices, for example, polyamide 6 [8], unsaturated polyester [9], reflected by the lower burning grade and limited oxygen index (LOI). Results show that polymeric matrices are easy to be ignited.

In order to prepare GFRPs with high flame retardancy, researchers have carried out a lot of researches [10,11]. Generally, two

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methods were adopted, one was adding flame retardant into resin matrices, and the other was grafting flame retardant onto GFs. For example, Liu's group prepared a kind of intumescent flame retardant (IFR) composing of ammonium polyphosphate (APP) and organic montmorillonite [12], which was then added into polypropylene to fabricate GFRPs. When the content of IFR in the matrix was about 18–25 wt%, the GFRP has high flame retardancy but deteriorated impact strength. Lim and his associates [13] fabricated two kinds of GFRPs with different matrices, one was original epoxy (EP) resin, and the other was modified EP resin by mixing with an IFR composing of APP and melamine cyanurate (MC). Results showed that the modification of EP resin could reduce the flammability of GFRPs to UL 94 V-1 grade; however, also bring 34.3 °C decrease in the initial degradation temperature ( $T_{di}$ ). Chen's group [14] incorporated phosphorus and nitrogen containing IFR into polyamide 6 (PA6), and prepared IFR/GF/PA6 composites. When the loading of IFR was about 30 wt%, the flammability of IFR/GF/PA6 composite was evaluated to be UL94 V-0 level; however, the impact strength of the IFR/GF/PA6 composite was only 53.0% of that of GF/PA6.

Due to the problems existing in the route of improving the flame retardancy through modifying resin matrices, several groups employed another method by modifying GFs. Liu's group used 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) grafted GF (GGF) as the reinforcement [15,16] to fabricate GGF/PA6 composites, and found that the modification of GF reduced the flammability of composites from no rating (NR) to UL-94 V-2 level and increased the impact strength with a degree of 8.3%. This group also compared GGF/EP and GF/EP composites, and found that the LOI value of GGF/EP was 10% higher than that of GF/EP composite, and heat release rate (HRR) had a 19.7% decrease; moreover, GGF/PA6 had 8.7% higher impact strength than GF/PA6, however no thermal property was provided.

These valuable literatures illustrate two important points. On one hand, the flame retardancy of a composite can be greatly improved by adding a large amount of flame retardant in the matrix, however this also obviously deteriorate the thermal stability and mechanical properties. On the other hand, the flame retardancy of composites can be improved through the surface treatment of GF; however, the amount of the grafted flame retardant on GF is generally limited, so the improvement degree of flame retardancy was not desirably high. Therefore it is interesting to explore new modification methods to develop novel GFRPs with remarkably higher flame retardancy without sacrificing thermal stability and mechanical properties.

Our project reported herein focused on this subject. Specifically, GF/vinyl ester (VE) composite was chosen as the model due to their wide applications [17,18]. Phosphorus-containing hyperbranched polysiloxane (PHSi) was synthesized as the flame retardant due to the good flame retarding effect of DOPO [19] and hyperbranched polysiloxane [20] as well as high thermal stability and good processing feature of hyperbranched polysiloxane. And then new GF fabric (PHSi-g-GF) grafted with PHSi through grafting-from technique, and new resin matrix consisting of PHSi and VE resin (coded as PSiVE) were prepared to develop three kinds of new composites (PHSi-g-GF/VE, GF/PSiVE, PHSi-g-GF/PSiVE). The structure and properties, such as flame retardancy, thermal stability, impact strength and interlaminar shear strength (ILSS), were systematically discussed and compared with those of GF/VE composite. Some interesting results were obtained, the origin behind was revealed, and consequently, a novel high performance GFRP was developed with simultaneously good flame retardancy, high thermal stability, impact strength and ILSS.

## 2. Experimental

### 2.1. Raw materials

Vinyltriethoxysilane (VTES) was purchased from Zhangjiagang Guotai Huarong New Chemical Materials Co., Ltd. (China). DOPO was bought from Eutec Chemical Co., Ltd (China). GF fabrics (3313: weight = 80 g/m<sup>2</sup>, thickness = 0.070 mm) were got from Asahi KASEI (Japan), which were dipped in acetone for 24 h and 10% HCl (aq) for 10 min at 60 °C, successively, to get clean GF fabrics. VE resin was obtained from Jiangmen Hengguang New materials Co., Ltd. (China). Methyl ethyl ketone peroxide (MEKP) was bought from Beijing Credit New Material Co., Ltd. (China). Propanol and concentrated NH<sub>3</sub>·H<sub>2</sub>O were commercial products and used as received.

### 2.2. Preparation of hybridized GF fabrics

Fig. 1 shows the procedures of preparing hybridized GF fabrics. Specifically, 10.0 g VTES, 0.164 g AIBN and 10.8 g DOPO were added into a 500 mL reactor with a magnetic stirrer and a reflux condenser under a nitrogen atmosphere. The temperature was kept at 80 °C for 8 h to obtain a light yellow liquid, coded as DTES.

0.1 mol DTES and H<sub>2</sub>O (the molar ratio of H<sub>2</sub>O to DTES was 1.1:1), 250 mL propanol and GF fabrics were added into a flask, the pH value of the solution was adjusted to about 10. After stirred at 50 °C for 6 h, the GF fabrics were taken out, washed with methanol for three times, and finally dried under vacuum at room temperature to get hybridized GF fabrics. These fabrics were coded as PHSi-g-GF and the grafting degree was measured to be about 2.04 wt%.

### 2.3. Preparation of PHSi and prepolymers

0.1 mol DTES, 0.11 mol H<sub>2</sub>O and 250 mL propanol were added into a flask, the pH value of the solution was adjusted to about 10. After stirred at 50 °C for 6 h, followed by removing the solution and the side-product (ethanol) under vacuum at 60 °C for 7 h, the resultant product was PHSi.

Appropriate quantities of VE and MEKP were blended with stirring, and then heated and maintained at 100 °C for 20 min to get VE prepolymer.

Appropriate amounts of PHSi, VE and MEKP were blended with stirring to get a homogenous solution, which was then heated and maintained at 100 °C for 20 min with stirring to obtain an uniform and transparent prepolymer, coded as nPSiVE, where n is the mass percentage of PHSi in PSiVE, taking values of 8 and 10. The Si–OH groups of PHSi will react with the active group (–OH) of VE resin during curing process.

### 2.4. Preparation of VE resin and composites

VE prepolymer was thoroughly degassed to remove entrapped air at 80 °C in a vacuum oven, and then cast into a mold for curing and postcuring following the protocol of 100 °C/1 h + 150 °C/2 h. The resultant product was cured VE resin.

Each VE or PSiVE prepolymer was dissolved in acetone (the weight ratio of the resin to acetone was 65:35) to form a transparent resin solution, named as varnish. A sheet of GF woven fabric was immersed in the varnish, and then hung up for at least 24 h at room temperature to remove acetone, followed by heating in a hot air convection oven at 130 °C for 10 min to form a prepreg.

The prepregs were stacked one by one, and then put into a metallic mold for molding according to a programmed cycle of 100 °C/1 h + 150 °C/2 h under a pressure of 100 psi. The resultant product was coded as GF/VE, PHSi-g-GF/VE, GF/10PSiVE, or PHSi-g-

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