



Development of the fire retardant glass fabric/carbonized phenolic composite



Minkook Kim, Jaeheon Choe, Dai Gil Lee*

School of Mechanical Aerospace & Systems Engineering, Korea Advanced Institute of Science and Technology, ME3221, Guseong-dong, Yuseong-gu, Daejeon 305-701, Republic of Korea

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ABSTRACT

Because fiber reinforced polymeric composite materials have the advantages of high specific strength and stiffness, their potential for replacing concrete, aluminum and steel. However, the poor fire resistance of fiber reinforced polymeric composite materials is one of the obstacles for their applications.

In this study, a fire retardant glass fabric/carbonized phenolic composite was developed using the carbonization of the phenolic resin. Although the glass fiber is not combustible, it melts at approximately 800°C on exposure to fire, whereas the phenolic resin has good fire resistance with minimum smoke levels, excellent dimensional stability and thermal strength. Moreover, the phenolic resin is carbonized at high temperature (above 500°C), which prevents the spread of flames. However, shrinkage during the carbonization process weakens its strength and stiffness.

To improve the pristine- and post-fire mechanical properties of the glass fabric/phenolic composite, flame and silane treatments were applied to the glass fabrics. The carbonization and impregnation of the phenolic resin matrix of the composite was repeated several times to develop the glass fabric/carbonized phenolic composite, from which the post-fire tensile strength and the carbonized phenol matrix ratio were measured with respect to the number of carbonization processes.

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1. Introduction

Fiber reinforced polymeric composite materials are widely used for a variety of applications due to their advantages; low density, high specific stiffness and strength, thermal insulation and low thermal expansion. In particular, glass fiber reinforced polymeric (GFRP) composites are extensively used in automotive and chemical industries and in marine applications because of their resistance to environmental and chemical attacks and their low cost [1]. Currently, GFRP composites are increasingly used in bridge and building construction in the form of sandwich structures [2,3].

A critical disadvantage of GFRP composite materials for buildings and other applications is poor fire resistance. Fire resistance is defined as the ability of a material to prevent the spread of fire (flame retardant) and maintain the mechanical properties in the event of fire (post-fire properties) [4]. At high temperature (typically above 300°C), most of the polymer matrices of composites decompose with the release of heat, smoke and toxic gases. The

most commonly used resins for the GFRP composites are epoxy, vinyl ester and polyester resins. However, these types of resins have short ignition times and low ignition temperatures in the event of fire and release large quantities of heat, smoke and toxic gases [5,6]. Moreover, the mechanical properties of load-bearing composite structures (e.g., walls, roofs) should be maintained during a fire to secure a safe space and an escape route. However, the stiffness and the strength of the composite materials are rapidly degraded by the damages from fire exposure. For example, the strength of the thin GFRP composites decreases more than 80% due to fire exposure [7,8]. The released heat and toxic smoke and the degradation of the structural integrity of the composites can cause serious injury and death [9,10].

Glass fibers are chemically stable and maintain their mechanical properties at high temperature. The softening temperature of E-glass fiber is approximately 850°C, and its melting point is approximately 1100°C [11]. Therefore, E-glass fiber has excellent fire resistance because the temperature of most fires is typically within the range of 500–1100°C [4]. Additionally, phenolic resins have good fire resistance, with minimum smoke levels, long ignition times, and lower yields of heat and toxic fumes. Phenolic resins are naturally transformed into char in fire due to the high aromatic content of 60 wt%. [12]. Therefore, E-glass/phenolic

* Corresponding author.

E-mail address: dglee@kaist.ac.kr (D.G. Lee).

URL: <http://scs.kaist.ac.kr> (D.G. Lee).

composites have some outstanding fire properties, such as low heat release rates and low toxic fume emissions. Because of the low cost and good fire resistance, glass/phenolic composites have been studied as alternate approaches to improve the fire resistance of GFRPs. However, the mechanical properties of the glass/phenolic composites are lower than other GFRPs because of the poor interfacial bonding strength between the glass fibers and the phenolic matrix and the low strength of the phenolic resin [13]. The tensile and flexural strengths can be severely degraded after being exposed to intense heat and fire [14]. The post-fire properties of glass/phenolic composites are degraded to less than 30% of the original stiffness and strength by fire exposure.

There are two major methods to improve the fire retardant property of the composites such as fire retardant fillers in the resin and fire protective surface coating, which will delay the onset and intensity of combustion and prevent the spread of flames. However, the post-fire properties of the composites with fillers and coating layers are much lower than the original strength, and most fire retardant fillers and coatings eventually ignite and increase the amount of heat, smoke and toxic fumes [15].

In this study, a fire retardant glass fabric/carbonized phenolic composite was developed using the carbonization of the phenolic resin. Flame and silane coupling agent treatments were used to improve the bonding strength between the E-glass fiber and the phenolic resin. To improve the fire resistance and post-fire mechanical properties of the glass fabric/phenolic composite, carbonization and impregnation of the phenolic matrix of the composite were repeated several times, from which the tensile strength and stiffness and the carbonized phenolic matrix ratio of the glass fabric/carbonized phenolic composites were measured with respect to the number of carbonization processes.

2. Experimental

2.1. Materials and fabrication process

The fire retardant E-glass fabric/phenolic composites were molded with a resole-type phenolic resin (KC-4703, Kangnam Chemical, Korea) and with an E-glass fabric. The properties of the resole-type phenolic resin are shown in Table 1. The reinforcement was a 1 k plain-weave E-glass fiber fabric (1180, Muhan Composite, Korea) with a thickness of 0.165 mm, a thread count of 0.95×0.95 per mm (24×24 thread count per inch) and an areal density of 0.176 kg/m^2 .

The glass fabric/phenolic composites were fabricated by the hand lay-up method and were cured by hot-compression molding under a curing pressure of 10 MPa at 160°C for 30 minutes. Eight plies of the glass fabrics were stacked, and the thickness of the composites was 1 mm. The fiber volume fraction (V_f) of the glass/phenolic composites was 60%.

2.2. TGA and DSC test

To investigate the chemical stability and reaction (carbonization or thermal decomposition) of the glass/phenolic composite

Table 1
Properties of the resole type phenolic resin.

Properties	KC-4703
Appearance	Liquid
Solids	60%
Solvent	Methanol
Curing temperature	120°C
Viscosity (#G @ 25°C)	A-E ($\approx 0.25 \text{ Pa}\cdot\text{s}$)
Gel time (@ 120°C)	15 min

with respect to the temperature, a thermo-gravimetric analysis (TGA) and differential scanning calorimetry (DSC) tests were performed. The mass losses of the glass/phenolic composite with respect to the temperature were measured by TGA test equipment (TG 209 F3, Netzsch, Germany). The heat generation rates in the dynamic scanning with respect to the temperature were measured by DSC test equipment (DSC 204 F1, Netzsch, Germany). The TGA and DSC tests were performed in a nitrogen (N_2) environment, and the temperature uniformly increased by 10°C per minutes from 25°C to 1000°C .

2.3. Post-fire tensile test

Tensile tests were performed according to ASTM D-3039 at room temperature to measure the tensile stiffness and strength of the glass fabric/phenolic composites. Fig. 1(a) shows the dimensions of the tensile test specimens. The sizes of the specimens were $100 \text{ mm} \times 15 \text{ mm} \times 1 \text{ mm}$ and 2 mm thickness end tabs were adhesively bonded to the specimens. The cut cross-sections of the specimens were polished to eliminate defects on the sides. The tensile tests were performed with a mechanical testing machine (Instron 4469, Instron, USA) with a test speed of 1 mm/min.

To investigate the fire resistance and the post-fire properties of the composites, a liquefied petroleum gas (LPG) burner was used. Fig. 1(b) shows an LPG flame burner for the fire exposure and burning test. The nozzle diameter was 1.0 mm, and the length of the burner was 600 mm. The flame treatment was performed with an inlet gas pressure of 25 kPa, and perfect combustion was achieved using a gas regulator for the LPG burner. The temperature of the LPG gas fire was 1000°C . The composite specimens were directly exposed to the LPG gas fire, and the tensile tests were performed with respect to the fire exposure time.

2.4. TMA test

Thermo-mechanical analysis (TMA) tests were performed to analyze the mechanical and dimensional stability of the composites. The strain of the glass/phenolic composite and the glass/carbonized phenolic composite was measured by TMA test equipment (TMA 402 F1, Netzsch, Germany) as a function of the applied force, temperature and time. A uniform tensile pressure of 50 kPa was applied to the 0.2 mm thick composite specimens, and the temperature was uniformly increased by 5°C per minute

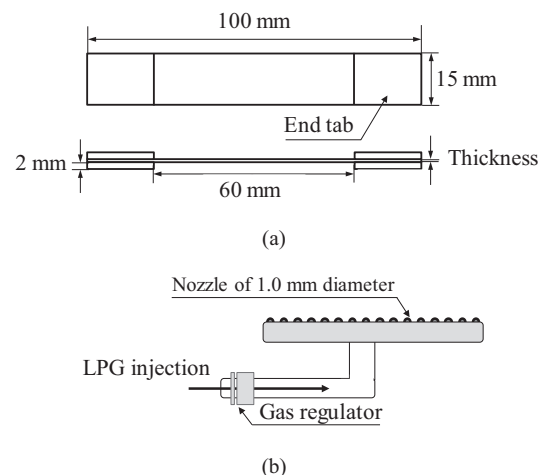


Fig. 1. (a) Dimensions of the tensile test specimens; (b) liquefied petroleum gas burner for the fire exposure test.

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