Composite Structures 147 (2016) 294–301

Contents lists available at ScienceDirect

Composite Structures

journal homepage: www.elsevier.com/locate/compstruct

Bonding characteristics between carbonized copper and a glass/phenolic composite

Seungjin Oh, Minkook Kim, Jaeheon Choe, Dai Gil Lee *

School of Mechanical Aerospace & Systems Engineering, KAIST, 291 Daehak-ro, Yuseong-gu, Daejeon 305-701, Republic of Korea

A R T I C L E I N F O

Article history:
Received 2 March 2016
Accepted 28 March 2016
Available online 29 March 2016

Keywords:
Carbonized layer
Glass/phenolic composite
Copper foil
Adhesive bonding

A B S T R A C T

Sandwich constructions composed of aluminum faces and a polymeric foam core generally have been used for thermal insulation structures for buildings. However, when fires occur, these sandwich constructions fail easily due to their low mechanical strength at high temperature and generate toxic gases during burning. Therefore, phenolic resin composites have been tried recently for fire retarding structures because of their low smoke generation level and good fire resistance due to the char generation on its surface.

In this study, copper foil was adhesively bonded to glass/phenolic composite faces to develop a fire retardant sandwich construction. To improve the adhesive bonding strength between the copper foil and the glass/phenolic composite, the carbonized layer method was developed. The pre-cured phenolic resin was carbonized and used as a primer. Finally, an optimum treatment condition of the carbonized layer method for the copper foil and glass/phenolic composite was investigated.

1. Introduction

Lightweight sandwich panels are widely adopted as structural components for various applications in marine, aerospace, automobile, transportation, and building constructions [1]. Conventional sandwich panels are composed of outer metal sheets and an insulation core material. For the insulation core material, polyurethane and polystyrene generally have been used [2,3]. However, conventional sandwich panels have low fire resistance because of the inflammable core material. The flame spreads rapidly, and the mechanical property of the conventional sandwich panels significantly decreases at the high temperature under the fire situation. In addition, toxic gases, such as carbon monoxide and hydrogen cyanide, are generated during burning [4–6]. Therefore, conventional sandwich panels are not suitable as a fire retardant construction.

In this study, a sandwich construction using phenolic resin was newly developed to replace the conventional sandwich panels. To ensure the safety of the sandwich panels in fire, it is composed of an inner phenolic foam core and copper foil which was bonded to the glass/phenolic composite face, as shown in Fig. 1. The glass/phenolic composite provides the mechanical properties of the panel and prevent the spreading of the flame [7,8]. Composites using phenolic resin have been proposed for fire retarding structures because of its low smoke generation level and high fire resistance due to the char generation on its surface [9,10]. In addition, phenolic resins have a high ignition point, low mass loss, low heat release rate, and low cost compared to other resins [11,12]. Glass fibers have been used for reinforcement materials because of their good thermal stability and low unit cost compared to other thermally stable fibers, such as aramid fibers [13–15]. The phenolic foam core insulates heat transfer because it has low thermal conductivity [11,16]. Therefore, combined glass/phenolic composites and the phenolic foam core has adequate fire resistance.

The glass/phenolic composites and the phenolic foam sandwich construction can effectively impede heat transfers by thermal conduction and convection. However, this sandwich construction cannot prevent the heat transfer through thermal radiation. At high temperature, a large proportion of the heat is transferred by thermal radiation because the energy flux of the thermal radiation E_b (W/m^2) is proportional to the fourth power of absolute temperature, T (K), as shown in Eq. (1), given by the Stefan–Boltzmann law [17,18].

$$E_b = \sigma T^4 \quad (1)$$

where σ (5.67×10^{-8} W/m^2 K^4) is the Stefan–Boltzmann constant. To improve the safety of the fire retardant structure, heat transfer through the radiation should be shielded.

* Corresponding author.
E-mail address: dglee@kaist.ac.kr (D.G. Lee).
URL: http://scs.kaist.ac.kr (D.G. Lee).

http://dx.doi.org/10.1016/j.compstruct.2016.03.048
0263-8223/

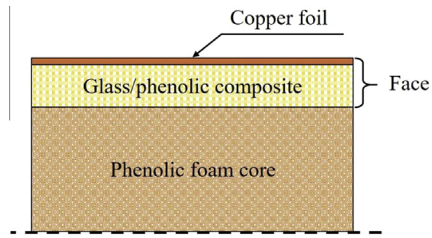

Fig. 1. Schematic diagram of a fire retardant sandwich construction.

Table 1
Thermal emissivity of the metals at 300 K and 1000 K.

Metallic solids (polished)	300 K	1000 K
Aluminum	0.04	–
Chromium	0.10	–
Copper	**0.03**	**0.04**
Gold	0.03	0.06
Silver	0.02	0.08
Stainless steel	0.17	0.30
Tungsten	–	0.10

There are two major methods to insulate the heat transfer by radiation: heat-insulation coating and metal sheet joining [19]. Because the heat-insulation coating using polymeric materials burns at the high temperature, the metal sheet joining method is appropriate for fire retardant constructions. In this paper, the mirror surface copper foil was joined to the front face of the glass/phenolic composite; which has low thermal emissivity and high melting point over 1000°C, as shown in Table 1 [18]. Stainless steel and aluminum have higher thermal emissivities compared to copper. In addition, the cost of gold and silver which have similar thermal emissivities are much higher than that of copper. For the adhesive joining method of the copper foil, a co-curing method was used to simplify the fabrication process and reduce the fabrication cost. However, the copper foil is difficult to bond with the glass/phenolic composite using a conventional adhesive co-curing method due to its low surface free energy [20].

To improve the bonding strength of metals, mechanical abrasions (such as sandpaper treatment, sand blasting, and plasma treatment) or chemical treatments (such as primer coating and coupling agent) generally have been used [21–25]. Mechanical abrasion methods improve the bonding strength by increasing the surface area; however, it has a limit for metals that have a low surface free energy, such as copper. In addition, chemical treatment methods are expensive and harmful to environment. Moreover, conventional surface treatment methods are not proper for high temperature application because their bonding properties drastically decrease at the elevated temperature. Therefore, a new surface treatment method that is cost effective and retains the bonding strength in the high temperature is required.

In this study, a new surface treatment method was developed and applied to the fire retardant construction. The adhesive bonding strength between the copper foil and the glass/phenolic composite was improved by generating the carbonized layer on the copper foil surface. The carbonized layer is chemically and mechanically stable at the high temperature of the fire situation. The optimum conditions of the carbonized layer generation were investigated with respect to the carbonization ratio. Next, the bonding strength between the copper foil and the glass/phenolic composite was investigated using the single-lap shear test. An optimum carbonization condition to enhance the bonding strength between the copper foil and glass/phenolic composite was determined.

2. Carbonized layer method

2.1. Concept of the carbonized layer method

Organic material can strongly bond to a metal surface via the carbonization process, such as a burned leftover food on the surface of a cooker. Organic material is condensed and joined to the metal surface strongly via dehydrogenation and dehydration reactions. In addition, the carbonized layer, which is mostly composed of carbon, has high bonding strength with polymeric materials. In the other words, by generating the carbonized organic layer on the copper foil, the bonding strength between the copper foil and the glass/phenolic composite could be improved. The phenolic resin, which has an organic group as shown in Fig. 2, was chosen to form the carbonized layer because it could be condensed to a combined carbon structure via the carbonization process. The carbonized phenolic resin layer strongly bonded to the copper foil surface by carbonization; this carbonized layer functioned as a bridge between the copper foil and glass/phenolic composite.

2.2. Fabrication process

The fabrication process of the carbonized layer method is presented in Fig. 3. To form a carbonized layer, the phenolic resin (KC-4703, KANGNAM chemical, Republic of Korea) was pasted onto the copper foil surface with a thickness of 10 μm, and it was cured by the vacuum bag degassing method in the oven. The curing temperature was 160°C, the curing pressure was 0.1 MPa, and the specimens were cured for 30 min. After the curing process, the cured phenolic resin layer was carbonized to different degrees by varying the carbonization time by propane gas flame. The propane gas flame was applied on the specimens by a propane gas burner, the nozzle diameter of 1.0 mm. The gauge pressure of the propane gas and the temperature of the flame were 25 kPa and 900°C, respectively. In addition, the distance from the propane gas flame to copper foil was 50 mm. During the carbonization process, temperatures were measured to investigate conditions of the carbonized layer. The carbonization temperatures were measured by the thermocouple instrument (NI 9211, National Instruments, United States) and the K-type thermocouples. The

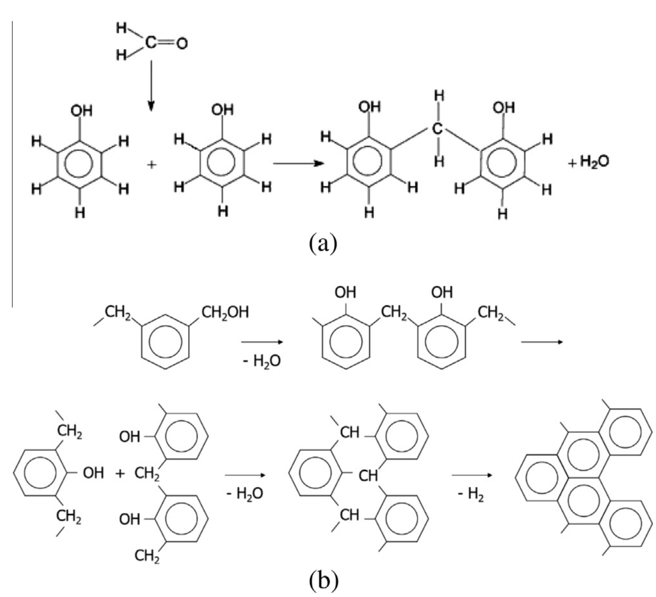

Fig. 2. (a) Curing process of the resole-type phenolic resin; (b) carbonization process of the phenolic resin.