Composite Structures 107 (2014) 522–527

Contents lists available at ScienceDirect

Composite Structures

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

Fracture toughness improvement of polyurethane adhesive joints with chopped glass fibers at cryogenic temperatures

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ARTICLE INFO

Article history:
Available online 30 August 2013

Keywords:
Polyurethane adhesive
Cryogenic temperature
Fracture toughness
Optimum reinforcement
Chopped glass fiber

ABSTRACT

Polyurethane (PU) adhesive is widely used for bonding the secondary barrier of cryogenic containment systems (CCS) of liquefied natural gas (LNG) ships due to its ductility at room temperature, although it can become brittle at the cryogenic temperature below its glass transition temperature.

To evaluate the reliability of PU adhesive at the cryogenic temperature of −150°C, the fracture toughness of double-cantilever-beam (DCB) adhesive joints composed of stainless steel and aluminum adherends was measured. Because the fracture toughness of the PU adhesive was found to be very low at the cryogenic temperature, the adhesive was reinforced with chopped glass fibers. The fracture toughness with respect to the length and volume fraction of the chopped glass fibers was then measured. Based on the experimental results, an optimal reinforcement method is suggested for the reliable application of PU adhesive at cryogenic temperatures.

1. Introduction

The demand for natural gas as an energy source has increased steadily, and natural gas is transported by pipeline systems and by ships all over the world [1,2]. For the purpose of efficiency, natural gas is largely transported in the form of liquefied natural gas (LNG) at −163°C by LNG ships. The cargo containment systems (CCS) for LNG ships must have cryogenic reliability under high thermal stress conditions.

Recently, membrane-type LNG containment systems have been widely employed for efficient and safe transportation of LNG [3,4]. A membrane-type LNG containment system is composed of dual barriers (primary and secondary barriers) against the leakage of LNG and insulation boards of sandwich construction for high thermal insulation, as shown in Fig. 1 [5,6]. Two LNG barriers (primary and secondary barriers) are employed. The former, which is in contact with the LNG, is usually made of metal plates without nil ductility, while the latter is a back-up barrier in the case of failure of the primary barrier. The secondary barrier should be able to maintain tightness for 15 days without leakage of LNG, according to the International Gas Carrier (IGC) code [7].

The secondary barrier is normally composed of sheet metals, such as aluminum sheets, which also serve as the faces of sandwich-type insulation boards, and stainless steel sheets, which serve as the overlying areas between the insulation boards. The two different types of metal sheets (aluminum and stainless steel) are usually bonded with polymeric adhesives. PU (polyurethane) adhesive is widely used to bonding sheets of two different types of metal because of its ductility at room temperature and its ability to fill large gaps. However, PU can become brittle at the cryogenic temperature below its glass transition temperature, as do other polymeric adhesives, such as epoxy adhesive [8–12]. It therefore might be necessary to reinforce PU adhesive to ensure high fracture toughness at the cryogenic temperature [13–17].

Several studies have been conducted to determine how to improve the fracture toughness of polymeric adhesives using various types of reinforcement. Zhao et al. [18] showed that E-glass fiber could stabilize crack propagation in DCB adhesive joints. Yoon et al. [19] investigated the effects of E-glass fiber reinforcement with respect to the fiber type, orientation and volume fraction in epoxy adhesive, using aluminum DCB adhesive joints at the cryogenic temperature. Hwang et al. [20] reinforced epoxy adhesive with E-glass and polyester fibers and found that they improved the fracture toughness of stainless steel DCB adhesive joints at the cryogenic temperature. Kim et al. [21] investigated the effect of aramid fiber reinforcement, considering the difference in the coefficient of thermal expansion (CTE) between adherends and adhesives at the cryogenic temperature.

However, most previous studies on this subject have been focused on the effect of fiber reinforcement on film-type epoxy

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0263-8223/$ - see front matter
http://dx.doi.org/10.1016/j.compstruct.2013.08.015

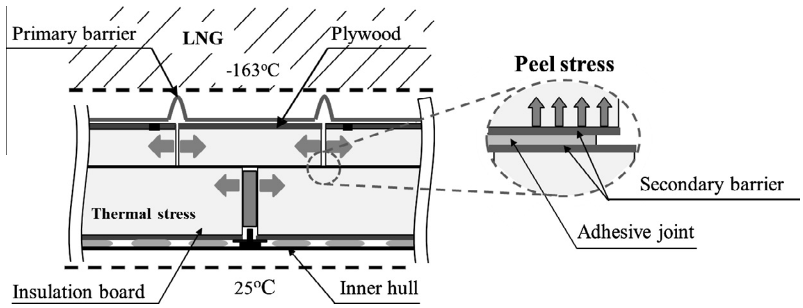

Fig. 1. Schematic diagrams of an LNG cargo containment system (CCS) subjected to thermal stress and peel stress.

adhesives for LNG containment systems. Only a few studies have been focused on liquid-type PU adhesive.

In this study, the PU adhesive was reinforced with chopped glass fibers to improve the fracture toughness of adhesive joints with aluminum and stainless steel adherends because chopped fibers can be easily mixed with a liquid adhesive using an automatic bonding machine for large bonding areas such as LNG CCSs.

To evaluate the fracture toughness of the adhesive joints, cleavage tests on the adhesively bonded DCB joints were performed at the cryogenic temperature of −150°C. From the test results, the energy release rate and crack resistivity of the joints were evaluated with respect to the length and volume fraction of the chopped glass fibers.

Lastly, an optimal method for reinforcing PU adhesive with chopped glass fibers was formulated to improve the fracture toughness of aluminum–stainless steel adhesive joints at the cryogenic temperature.

2. Experiment

2.1. Surface treatment for metal adherends

The surfaces of the aluminum and stainless steel blocks used in this study were cleaned with acetone to remove lubricants and dirt particles absorbed during the manufacturing process. Then, a flame treatment with propane gas was performed to remove remaining oil and dirt particles and increase the surface energy of the adherends. Lastly, the flame-treated metal adherends were immersed in a 0.1% silane solution for 10 min and dried in a hot chamber [14].

2.2. Fabrication of double-cantilever-beam (DCB) adhesive joints

To measure the Mode I fracture toughness of DCB adhesive joints bonded with PU adhesive, adhesive joints were prepared in accordance with the ASTM D3433 standard, as shown in Fig. 2 [22]. Because an adhesive joint is composed of two different materials, such as aluminum and stainless steel, a DCB joint is asymmetric with respect to the adhesive layer when the same thicknesses are used for the two adherends. Therefore, the thicknesses of the adherends were adjusted, which is a slightly departure from the ASTM D3433 standard, to make the flexural rigidities of the two adherend structures the same, as shown in the following equation:

$$(EI)_{\text{aluminum}} = (EI)_{\text{stainless steel}} \tag{1}$$

The thicknesses of the aluminum and stainless steel adherends were 17 mm and 12 mm, respectively. The adhesive in the joint was cured using a hot press at 70°C for 2 h, and an adhesive thickness of 0.5 mm was maintained by placing a thickness gage between the adherends. A fresh razor blade was inserted in the adhesive during the curing process and tapped to generate a sharp initial crack tip in the cured adhesive [23–25].

2.3. Fabrication of chopped glass fiber-reinforced PU adhesive

The PU adhesive used (XPU 18045, Bostik, France) has a density of 1300 kg/m^3 and a viscosity of 26,000–30,000 mPa s at a room temperature of 25°C, which is a very viscous liquid. To reinforce the adhesive with a high volume fraction of chopped glass fiber, the adhesive was heated to lower its viscosity, as shown in Fig. 3. The dual-type liquid PU adhesive was composed of polyol and isocyanate, the viscosities of which are 30,000 mPa s and 26,000 mPa s, respectively, at room temperature. They were heated in a chamber at 60°C for 30 min to reduce their viscosities, and then chopped glass fibers were dispersed into them. Prior to mixing of the polyol and isocyanate with the chopped glass fibers, they were heated again in a chamber at 60°C for 30 min to decrease their viscosities. Lastly, the reinforced polyol and isocyanate were mixed to be dispensed on the adherends.

2.4. Double cantilever beam (DCB) test

The cleavage DCB test was performed to evaluate the fracture toughness of adhesive joints reinforced with chopped glass fibers

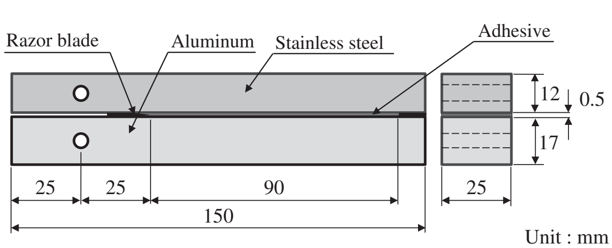

Fig. 2. Schematic drawing of an adhesively bonded DCB joint specimen composed of aluminum and stainless steel adherends.

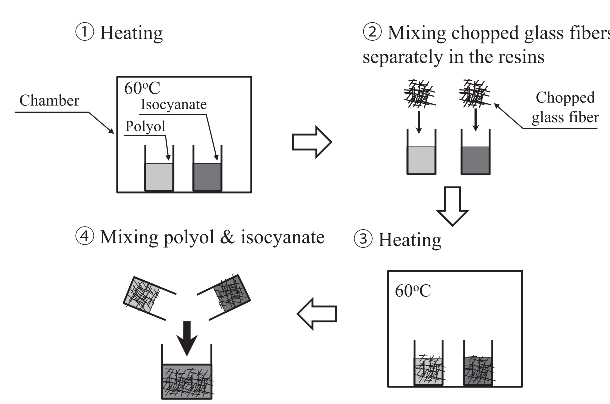

Fig. 3. Schematic diagram of the fabrication process for chopped glass fiber-reinforced PU adhesive.