Enhancement of the crack growth resistance of a carbon/epoxy composite by adding multi-walled carbon nanotubes at a cryogenic temperature

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Abstract

The improvement of crack resistance is essential to the application of fiber reinforced composites for cryogenic use. In this study, the authors attempted to enhance the crack resistance of a carbon/epoxy composite by adding multi-walled carbon nanotubes (MWNTs) into the resin formulation. Prior to assessing the effect of MWNTs, the effect of a toughened epoxy resin on the mode I interlaminar fracture toughness was investigated at \(-150\, ^\circ\text{C}\) using double cantilever beam (DCB) specimens. It was found that the degree of fracture toughness enhancement obtained from application of the toughened epoxy at cryogenic temperature was less than that at room temperature, due to embrittlement of the epoxy resin. MWNT-added carbon/epoxy unidirectional prepregs were fabricated via a filament winding method with different concentrations of MWNTs (0.0 wt% for baseline, 0.2 wt% and 0.7 wt%). Material systems blended with 0.2 wt% and 0.7 wt% of MWNTs showed enhanced fracture toughness and low crack density at the cryogenic temperature.

Keywords: A. Nano-structures; B. Fracture toughness; B. Transverse cracking; D. Mechanical testing; Cryogenic temperature

1. Introduction

Carbon fiber reinforced composites are considered as promising materials for application in fuel tank structures of launch vehicles due to their favorable mechanical characteristics like high specific strength and specific stiffness. Furthermore, cryogenic liquids such as liquefied oxygen and liquefied hydrogen are often used as an oxidizing agent and fuel, respectively, owing to their high specific impulse measures [1]. When a composite tank is used to store cryogenic liquids, it undergoes cryogenic aging as well as cycling from room temperature to cryogenic temperature as a load is added. Microcracks can then grow in the composite matrix due to the difference in the coefficients of thermal expansion of the fiber and matrix and between different angle layers. Such structural damage gives rise to a degradation of mechanical properties in the structures, such as fiber/matrix interfacial debonding, potholing, and/or delamination, all of which are likely to result in leakage of liquids [2,3].

Since the development of toughened polymer resins, many researches have addressed the advantages and drawbacks of these materials as matrices for composites. In particular, toughened epoxy resins incorporated with micro/nano-sized rigid fillers such as alumina and clay show enhanced crack growth resistance when applied in fiber reinforced composites [4,5]. With regard to cryogenic applications, some studies have examined the crack density and its propagation after applying cryogenic cycles on carbon fiber reinforced composites having different fiber and resin
compositions \[6,7\]. Also, it has been demonstrated that delamination or crack resistance can be improved by employing nano-sized Al\(_2\)O\(_3\) particles \[8\] and clay \[9,10\] at cryogenic temperature.

Carbon nanotubes (CNTs) have exceptional mechanical properties as well as a high aspect ratio with large specific surface area, making them a promising reinforcing material for polymer matrix composites \[11–13\]. Some previous works \[14,15\] showed that CNTs can be employed as an alternative reinforcing filler to enhance not only mechanical properties but also crack growth resistance, as they can serve as bridges between crack surfaces and induce mechanical interlocking with the matrix material. Recently, it was shown that the combination of a CNT-modified matrix together with conventional fibre-reinforcements can lead to improved matrix-dominated properties such as interlaminar shear strength \[16\].

This study aims at improving the crack growth resistance of a carbon/epoxy composite at a cryogenic temperature by employing multi-walled carbon nanotubes (MWNTs) in the resin formulation. First, the effects of toughened epoxy resin on the mode I interlaminar fracture toughness were investigated at room temperature (RT) and at \(-150\) °C. Subsequently, MWNT-added carbon/epoxy unidirectional prepregs were fabricated with different concentrations of MWNTs. Mode I interlaminar fracture toughness was compared for each MWNT-added specimen at the cryogenic temperature. Finally, the effect of MWNTs on the crack resistance was investigated by measuring crack density after six thermo-mechanical cycles from RT to \(-150\) °C.

2. Experiments

2.1. Comparison of the toughening effect

2.1.1. Material system

Table 1 shows the resin composition of carbon fiber reinforced composites developed for cryogenic use in a previous study \[17\]. The resins of each composite material were formulated using a mixture of commercial epoxy resins. Aliphatic polyamine dicyandiamide (DICY) was used as a hardening agent and diuron (DCMU) was used as an accelerator for curing. Also, a carbon fiber, T700 from Toray Industries Inc., was used for reinforcement in each composite material.

In Table 1, CU125NS, as a baseline material, is a carbon/epoxy prepreg model manufactured by Hankuk Fiber Glass Corporation (South Korea) by way of a hot-melting process. Type B material was formulated with the same epoxy resin as in CU125NS but with a different blend ratio. CU125NS contains more phenolic novolac epoxy resin than bisphenol-A epoxy resin in the resin composition, while Type B has more bisphenol-A epoxy resin, which is expected to lend stress–relaxation capability to their molecules at cryogenic temperature \[18\]. Also, carboxyl terminated butadiene acrylonitrile (CTBN) modified rubber was incorporated into the resin mixture of the Type B model as a toughening agent.

2.1.2. Specimen preparation

The toughening effect of the prepreg models was investigated by comparing their mode I interlaminar fracture toughness using a double cantilever beam (DCB) test. Fig. 1 shows the configuration of the DCB specimen.

The specimen configurations and test procedures were in accordance with ASTM D 5528. Each laminate in the two models was stacked with \([0]_{40T}\), respectively. A non-adhesive insert (Teflon film A4000, Airtech International Inc.) of a thickness of 25 μm was inserted in the midplane of the laminate during the lay-up to form an initiation site for delamination. Each prepreg was cured in an autoclave with a two-stage cure cycle, maintaining a temperature of 80 °C
for 30 min followed by 130 °C with 700 kPa for 2 h. After curing, aluminum alloy (Al-6061) blocks were attached on the two edges of the laminate with FM123 adhesive film in an autoclave at a temperature of 120 °C for 2 h.

2.1.3. Test procedure and evaluation method

In this study, an environmental test chamber was used to simulate a cryogenic environment. The temperature of the environmental chamber (Instron 3119-407) was lowered to −150 °C by evaporating liquid nitrogen (LN2). The chamber was equipped with an Instron 4202 and sealed with an insulating material. Fig. 2 shows the setup of the DCB test in the chamber. DCB grips and loading bars of the apparatus were inserted into the chamber. The time needed to lower the temperature generally depends on the pressure level of the vessel containing the liquid medium. Accordingly, the use of a pressurizing device helped maintain an evaporating pressure of 1.5 atm. (22 psi) and kept the cooling time constant.

In the DCB test, the delamination growth length, which propagated during loading, was observed using a traveling optical microscope (∼40). In most cases, a resin rich area was found at the tip of the insert of the DCB specimen, and therefore a precrack of 5 mm was created before the test.

Eq. (1) presents the definition of the potential energy release rate per unit length of crack creation ($G$). $W_L$ and $U_E$ represent the work done by external force and stored strain energy, respectively, and $\Pi$ denotes the potential energy

$$G = \frac{-\partial (W_L + U_E)}{\partial a}$$

In this study, the mode I interlaminar fracture toughness, $G_I$, was calculated through a modified beam analysis method, taking the rotation at the delamination front into account. Eq. (2) shows the calculation of $G_I$ described in ASTM D 5528

$$G_I = \frac{3P\delta}{2b(a + |\Delta|)}$$

A constant crosshead rate of 1 mm/min was applied during the test and crack growth length was continuously observed via CCTV, which was connected to the traveling optical microscope. The load ($P$) and the displacement ($\delta$) were recorded at every 5 mm of crack growth length ($a$). In

Fig. 2. DCB test setup and monitoring the crack propagation via CCTV: (a) CCTV monitor and (b) DCB setup.
Eq. (2), \( b \) denotes the specimen width. The correction factor \( (D) \) was obtained by applying a least square fit to a graph of 1/3 power of the compliance versus crack length.

2.1.4. Results

Potential energy release rate, \( G_{IR} \), is shown as a function of crack length at RT and at \(-150^\circ C\) in Fig. 3. Typical resistance curves (\( R \)-curves) are found at RT for both the CU125NS model and Type B model. At \(-150^\circ C\), however, these models do not show typical \( R \)-curve behavior. In other words, \( G_{IR} \) is nearly independent of the crack growth length. This indicates that the crack growth became unstable soon after initiation. This behavior was attributed to a reduction of the fiber bridging effect and a decrease of the process zone in the wake of the crack surfaces. Fig. 4 shows the fractured surface of the DCB specimens at RT and \(-150^\circ C\), respectively. From observation of the fractured surfaces, it is estimated that the cracks propagated with a little fiber/matrix interfacial debonding failure at \(-150^\circ C\) relative to those at RT. As a result, the fiber bridging effect could be reduced at \(-150^\circ C\).

Another reason for the unstable crack growth at the initiation time could be the decrease of the process zone in the wake of the crack surface. Du [19] showed that \( R \)-curves are directly correlated to the evolution of the process zone during steady-state crack propagation in an epoxy resin system. Thus, it is estimated that a decrease of the process zone caused the crack propagation to progress more rapidly at \(-150^\circ C\) than at RT.

In this study, mode I interlaminar fracture toughness was compared in terms of steady-state propagation fracture toughness obtained during unstable crack growth. This approach was taken because the crack propagated rapidly at \(-150^\circ C\) upon initiation of the DCB test. Therefore, it was difficult to measure the initial fracture toughness, and thus a reasonable comparison of the fracture toughness at RT and that at \(-150^\circ C\) could not be made. The propagation fracture toughness is shown in Fig. 5 for CU125NS and Type B, respectively. Type B shows higher fracture toughness than CU125NS both at RT and \(-150^\circ C\). This increase in fracture toughness is attributed to the toughening effect of bisphenol-A epoxy resin and CTBN modified rubber. However, the enhancement of fracture toughness by the toughened epoxy was reduced from a 160% increase at RT to a 97% increase at \(-150^\circ C\). This result appears to be attributable to embrittlement of the polymer resin at cryogenic temperature. Consequently, it was concluded that the degree of crack resistance enhancement by a toughened epoxy system incorporated with rubber is reduced at cryogenic temperature relative to that at RT.

2.2. Fracture toughness of MWNT-added carbon/epoxy composite

2.2.1. Fabrication

As noted in the former section, the toughening effect obtained by using the toughened epoxy is reduced at cryogenic temperature due to embrittlement of the epoxy resin. In this study, therefore, multi-walled carbon nanotubes (MWNTs), a nano-filler, are employed to improve the fracture toughness of a carbon/epoxy composite at cryogenic temperature. To date, many papers have reported that MWNTs can improve the mechanical and electrical properties of polymer matrix composites. Moreover, MWNTs show high slenderness and specific surface area (\( \sim 200 \text{ m}^2/\text{g} \)) [20], making them suitable reinforcing filler candidates.

MWNT-added carbon/epoxy unidirectional prepregs were manufactured via a filament winding method. During their manufacture, carbon fiber (T700, Toray Industries) was used as reinforcement in the form of rovings (12 K), and the Type B epoxy system was utilized as the binding matrix. MWNTs used in this study, purchased from Iljin Nanotech Corporation (South Korea), were synthesized.
via a chemical vapor deposition (CVD) method. The MWNTs are 10–20 nm in diameter and 10–50 μm in length.

Three kinds of prepregs were manufactured by Hankuk Fiber Glass Corporation (South Korea), each having a different percent of MWNT addition into the resin, i.e., 0.0 wt% (MWNT0.0), 0.2 wt% (MWNT0.2), and 0.7 wt% (MWNT0.7) of the resin weight. The fabrication process for the MWNT-added carbon/epoxy prepreg is as follows: first, MWNTs were dispersed in an acetone solvent using a direct driven stirrer for 2 h. The suspension and Type B toughened epoxy resin were then mixed together by mechanical stirring. Subsequently, a hardening agent (DICY) and accelerating agent (DCMU) were mixed into the MWNT-added Type B resin. In the filament winding process, carbon fiber rovings impregnated into the pre-mixed resin bath were wound onto a mandrel which had 1.4 mm diameter with a controlled winding tension of 1.5 kgf. Mechanical stirring was continuously performed during the winding. After winding, the prepregs were held at 20 °C for 2 h and then cut to proper size. Each laminate of the MWNT-added prepregs was stacked with [0]_{16T} to obtain the same thickness as the standard specimen in ASTM D 5528. The DCB specimen configuration and test procedure are described in Sections 2.1.2 and 2.1.3.

2.2.2. Results and discussion

Fig. 6 shows typical R-curves obtained from a DCB test for different weight percent of MWNTs both at RT and −150 °C. It is observed that the R-curves show different behaviors at RT and at −150 °C. In addition, the R-curves of the DCB specimens fabricated by the filament winding method show a wider stable crack growth region at −150 °C relative to those fabricated by a hot-melting method, as shown in Fig. 3. This difference is due to the degree of fiber alignment for the specimens fabricated by the filament winding method being lower than that of the specimens fabricated by hot-melting, and thus in the former there is a stronger fiber bridging effect on the fracture toughness.

In Fig. 6, the stable crack growth region, which is characterized by a curvilinear shape, is more widely distributed along the crack length at RT than at −150 °C. This indicates that unstable crack propagation occurs under a lower crack driving force at cryogenic temperature than at RT. This is due to embrittlement of the epoxy matrix at the cryogenic temperature, which decreases the crack resistance of the composite. In addition, it is found that MWNTs have little influence on the R-curve behavior at RT, but a considerable influence at the cryogenic temperature. Therefore, it can be concluded that cracks can propagate stably under higher crack driving force by the addition of MWNTs at cryogenic temperature.

As noted in Section 2.1.4, it is unreasonable to compare the initiation fracture toughness at −150 °C because of the rapid crack propagation velocity. Moreover, even though the steady-state propagation fracture toughness is similar at both temperatures, the work of fracture at the same crack length could be different. As shown in Fig. 6b, it is found that MWNT0.2 shows similar steady-state fracture toughness with MWNT0.7 in spite of a lower driving force in the stable crack growth region for equal crack length. Therefore, in this study, the work of fracture was evaluated to compare the crack resistance of MWNT-added DCB specimens. The potential energy also can be considered as dissipation energy during crack propagation. Thus, the dissipation energy was obtained by integrating the R-curves for the stable crack growth region (65 < a < 100) in Fig. 6. For this calculation, a sigmoidal curve (Boltzmann function, $R^2 > 0.95$) was adopted to fit the R-curves and integration was performed using OriginPro 6.1 commercial software.

The calculated dissipation energy for the MWNT-added DCB specimen is graphically illustrated in Fig. 7. It is found that all the laminate composites show a decrease in the dissipation energy to the crack propagation at cryo-
genic temperature. In other words, lower energy (or driving force) is needed for the crack propagation, which is indicative of a reduction of fracture toughness. The MWNT0.7 specimen shows the highest dissipation energy, both at RT and at −150 °C. At these temperatures, the dissipation energy is 6.4% and 30.8% higher, respectively, than that of the baseline (MWNT0.0) specimen. Therefore, it can be considered that employing MWNTs as a filler is an effective strategy to obtain high fracture toughness with regard to the application of composites in cryogenic use.

2.2.3. Fractography

Fracture surface of the DCB specimens was observed by scanning electron microscopy (SEM). Fig. 8 shows the fracture surface of the MWNT0.0 specimen and MWNT0.7 specimen at −150 °C. In this study, agglomerated MWNTs in a size range of several μm to dozens of μm were observed. The MWNT0.0 specimen fractures with a smooth crack surface while the MWNT0.7 specimen displays a relatively rougher fracture surface. A rough fracture surface is evidence that high dissipation energy is required for crack propagation [9]. This result is attributed to the addition of MWNTs, which induce interlocking failure with the matrix material, and thus more fracture energy is needed to create the crack surface.

2.3. Measurement of the crack density

The effect of MWNT addition on crack resistance was investigated by measuring the crack density after a thermo-mechanical loading cycle from RT to −150 °C. Laminated cross-ply specimens with a sequence of [0°/90°]s were fabricated using different MWNT-added pre-pregs, as shown in Fig. 9.

The thermo-mechanical cycle was carried out in the environmental chamber. The cyclic load was applied to the cross-ply specimen up to 14 kN, which was half of the failure load of the specimen at RT. After the temperature was lowered to −150 °C, thermal equilibrium of the...
specimen was maintained for nearly 30 min. The crack density was observed after six thermo-mechanical cycles through an optical microscope (PME3, Olympus) and was defined as the number to the measuring span length (the number of transverse crack/Cm) \[7\]. The crack densities were averaged over a 60 mm span on the 90°/C176 layers, as shown in Fig. 9. The crack densities are compared by weight percent of the MWNTs in Fig. 10. Both the MWNT0.2 and MWNT0.7 specimens show lower crack density than the MWNT0.0 specimen. These results show good agreement with the enhancement of fracture toughness observed upon the addition of MWNTs at -150°C, shown in Fig. 7.

3. Conclusion

The toughening effect of a carbon/toughened epoxy on the Mode I interlaminar fracture toughness was investigated at -150°C using double cantilever beam specimens. It was found that less enhancement of fracture toughness by the toughened epoxy was obtained at cryogenic temperature than at RT. This result is mainly attributable to embrittlement of the epoxy resin at the lower temperature.

The authors attempted to improve the crack resistance of a carbon/epoxy composite by adding MWNTs into the resin formulation. The crack resistance was evaluated by comparing the dissipation energy for Mode I interlaminar fracture. The integration of MWNTs resulted in a rough fracture surface in the matrix region. Consequently, material systems blended with 0.2 wt% and 0.7 wt% of MWNTs showed lower crack density than the baseline specimen.

References


