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Paper

Inter-lamina Shear Strength of MWNT-reinforced Thin-Ply CFRP under LEO Space Environment

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ABSTRACT: In this paper, the inter-lamina shear strength (ILSS) of multi-wall carbon nanotube (MWNT) reinforced carbon fiber reinforced plastics (CFRP) and thin-ply composites were verified under low earth orbit (LEO) space environment. CFRP, MWNT reinforced CFRP, thin-ply CFRP and MWNT reinforced thin-ply CFRP were tested after aging by using accelerated ground simulation equipment. The used ground simulation equipment can simulate high vacuum (2.5×10^{-6} torr), atomic oxygen (AO, 9.15×10^{14} atoms/cm^2·s), ultraviolet light (UV, 200 nm wave length) and thermal cycling (-70~100°C) simultaneously. The duration of aging experiment was twenty hours, which is an equivalent duration to that of STS-4 space shuttle condition. After the aging experiment, ILSS were measured at room temperature (27°C), high temperature (100°C) and low temperature (-100°C) to verify the effect of operation temperature. The MWNT and thin-ply shows good improvement of ILSS at ground condition especially with the thin-ply. And after LEO exposure large degradation of ILSS was observed at MWNT added composite due to the thermal cycle. And the degradation rate was much higher under the high temperature condition. But, at the low temperature condition, the ILSS was largely recovered due to the matrix toughening effect.

Key Words: Low Earth Orbit, Atomic oxygen, High vacuum, Ultra-violet light, Thermal cycling, Multi-walled carbon nanotubes (MWNTs), Thin-ply, Composites

1. INTRODUCTION

The main advantages of carbon fiber reinforced plastics (CFRP) are the high specific strength and stiffness as well as their low thermal expansion coefficient which results in dimensional stability. These characteristics appropriately satisfy the requirement of spacecraft. Due to this reason, composite materials have been widely used as structural materials of space vehicles. In spite of these merits, there are some problems in applying composite materials to low earth orbit (LEO) space environment, because the operating environment is extremely different from that of ground. In contrast with the ground environment, the LEO space environment has many harsh constituents, such as high vacuum (10^{-6}~10^{-10} torr), ultraviolet (UV, wave length 100~200 nm) radiation, high thermal cycles (-150~150°C), atomic oxygen (AO, with kinetic energy of 5 eV, nominal AO flux about (10^{14}~10^{15}) atoms/(cm^2·s)), charged particles, electromagnetic radiation, micrometeoroids, and man-made debris [1]. Polymers and polymer matrix composites (PMC) experience the erosion of surface, mass loss and degradations of their material properties under the LEO environment [2-4].

Ground simulation experiments have been done to verify the property changes of polymer films and PMC induced by individual components of the harsh LEO environment [1,5-8]. At the ground simulation experiment, the similar damages were observed at the polymer matrixes and films by the simulated harsh LEO environmental factors, especially the AO attack. When the adverse factors are simultaneously applied in a combination of two or three, the aging rates were much higher than those by the individual LEO environmental factor due to the synergistic effects [1,9]. Therefore, characteristics of the polymer matrix composite should be understood under the whole components of the LEO space environment simul-

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taneously applied case. In advance, the research on the methods to protect composite materials from the LEO space environment must be done.

SiO_2, Al_2O_3, indium tin oxide (ITO) and diamond-like carbon (DLC) coatings, the ion implantation method have been studied to protect the surface of polymer and PMC [10-16]. These coating methods are effective in improving the resistance against the LEO environment at the initial stages. However, coating methods are not effective in the long term due to the torch-blow effect induced by cracks, undercutting and separation from the polymer coating surface [17]. Therefore, the different concept to improve the properties and resistance of the CFRP (carbon fiber reinforced plastics) are necessary.

Carbon nanotubes (CNTs) are the one of promising material to improve the composite material properties especially the out-of plane properties such as interlaminar shear strength (ILSS) and the interlaminar fracture toughness of layered composites. Because CNTs can serve as bridging material between crack surfaces and can induce mechanical interlocking with the matrix material, they can enhance the mechanical properties and crack growth resistance [18-22]. CFRP laminates manufactured from thin-ply prepregs have high damage resistance characteristics compared to standard prepregs due to its high constraining effect [23,24].

In this paper, MWNT and thin-ply are suggested and tested under different environment conditions, namely simulated LEO space environment and ground condition to improve the ILSS of the composites.

2. EXPERIMENT

2.1 Fabrication of prepreg

Four different kinds of prepreg models were prepared to verify the effect of MWNTs as to the reinforcement and prepreg thickness as shown in Table 1. The resins of each composite material were formulated using a mixture of commercial epoxy resins.

Each prepreg model was manufactured by Hankuk Fiber Glass Corporation (South Korea) via a hot-melting process. CN, as the baseline material, is the commercial carbon/epoxy unidirectional prepregs with a thickness of 0.125 mm. CT has half the thickness (0.060 mm) of the CN prepreg. MWNT-CN and MWNT-CT are 3-phase carbon/epoxy unidirectional prepregs reinforced with functionalized MWNTs with different ply thicknesses.

Table 1. Carbon/epoxy prepreg models

Denotation	Material description	Ply thickness	Remark
CN	CU125NS	0.125 mm	Baseline
CT	CU050NS	0.060 mm	Thin ply
MWNT-CN	CU125NS + 0.7 wt% MWNTs	0.125 mm	MWNTs reinforced
MWNT-CT	CU050NS + 0.7 wt% MWNTs	0.060 mm	MWNTs reinforced thin ply

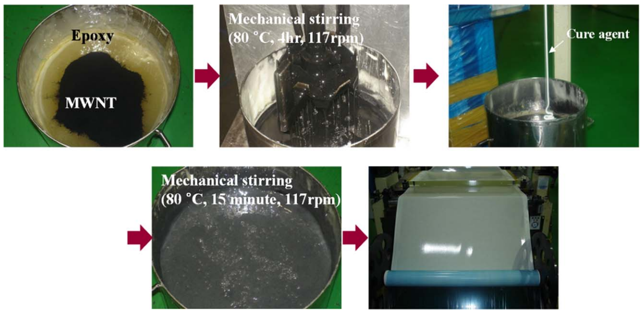


Fig. 1. Fabrication process of 3-phase UD prepreg

During their manufacture, carbon fiber (T700, Toray Industries) was used as the primary reinforcement and the resin was formulated using a mixture of phenolic novolac epoxy and bisphenol-A epoxy as the binding matrix.

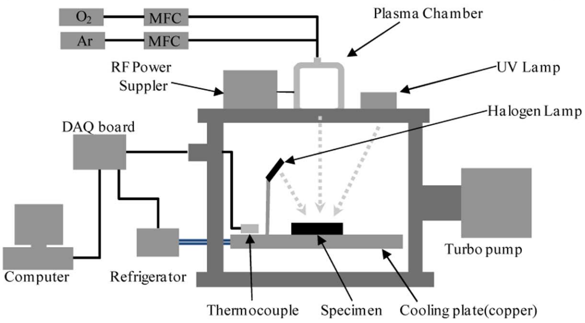
The MWNTs used in this study, purchased from Iljin Nanotech Corporation (South Korea), were synthesized via a chemical vapor deposition (CVD) method. The MWNTs are 10~20 nm in diameter and 10~50 μm in length. MWNTs were purified with a mixture of sulfuric (98%) and nitric (68%) acids and subsequently functionalized with TETA (triethylenetetramine) to induce covalent bonds between amino-functionalized group and epoxide. The detail information about the procedure and the result of functionalization is reported in the paper [18]. Amino-functionalization is a popular chemical treatment to realize good interfacial bonding between epoxy resin and CNTs. The fabrication process for the MWNT-added 3-phase carbon/epoxy prepreg is shown in Fig. 1. First, functionalized-MWNTs were directly poured into the epoxy resin and subsequently stirred at 80°C for four hours. After mechanical stirring, a hardening agent was mixed into the MWNT-added epoxy resin through mechanical stirring for fifteen minutes. Finally, MWNT-added 3-phase carbon/epoxy prepreg was fabricated by way of a hot-melting process.

2.2 Experimental setup

An accelerating LEO space environment simulating equipment was used to simulate the aging of composites under LEO space environment condition. This equipment can simulate high vacuum (2×10^{-6} torr), AO (with 0.04 eV kinetic energy), thermal cycling (-70~100°C), and UV radiation (200 nm wavelength) simultaneously. Fig. 2(a) shows a picture of equipment and Fig. 2(b) shows a schematic diagram of the simulation equipment chamber.

This equipment can make a high vacuum (2×10^{-6} torr) by using a diffusion pump. And the atomic oxygen is generated from the mixture of oxygen and argon gases which are fed into the plasma chamber located on the top of the main chamber.

(a) Picture of the accelerated LEO simulation facility



(b) Schematic diagram of the LEO simulation chamber

Fig. 2. Facility of accelerated LEO space environment simulation

RF power (600 W, 13.56 MHz) is supplied to the mixture of two gases to generate plasma. By using the generated oxygen plasma, an AO condition can be realized [1]. In the main chamber, a flat copper plate is located that can be cooled down to -70°C by the refrigerant circulating inside the copper plate. A halogen lamp that is able to warm up the specimen to 100°C was used as a heating system. The period of one thermal cycle was measured about 1.4 hours. Specimens were exposed to UV light by using a UV lamp located on the top of the main chamber. This lamp was turned on during heating time because UV radiation and heating occur simultaneously in orbit due to radiation from the sun.

To identify the capacity of the facility, a calibration test was performed. Kapton film, as a baseline material, was used as specimen. Kapton is one of the most studied materials susceptible to AO degradation in the LEO environment. Therefore, Kapton is often considered as a reference standard for comparison between ground-simulation laboratory tests and flight experiments [25]. In this calibration experiment, 30 mm × 30 mm Kapton films were used as specimens and aged in the facility for eight hours under LEO conditions. High vacuum, AO, UV light and thermal cycling were simultaneously applied. After aging, the mass loss of the Kapton film was measured, and by using Eq. (1), the equivalent AO flow rate was calculated.

$$AO\ flow\ rate = \frac{M_I - M_F}{\rho \times A \times t \times AORC} \tag{1}$$

In this equation M_I, M_F are the initial and the final mass of Kapton film, and ρ, A and t are the density, the exposed area of a specimen and the exposure time. The *AORC* is the atomic oxygen reactivity coefficient, which refers to the flight test result value, 2.8×10^{-24} cm^3/atom [25].

The calculated equivalent AO flow rate was 9.15×10^{14} atoms/(cm^2·s). This value was used to calculate the main experiment duration in order to simulate space shuttle mission condition (STS-4) by ground experiment. During an STS-4 mission, the total AO quantity directed at the space shuttle during operation is 0.65×10^{20} atoms/cm^2 [25]. The total exposed AO was divided by calculated equivalent AO flow rate, and then experiment time was calculated. To simulate STS-4 conditions, this facility required twenty hours of operation [26].

2.3 LEO exposure experiment

To verify the synergistic effect of LEO environment on the composite, four constituents of LEO space environment were applied simultaneously for twenty hours. During the experiment, the vacuum pressure was maintained with 2.9×10^{-6} torr. And AO was constantly sprayed during the whole the duration. Fourteen times thermal cycles (-70~100°C) were repeated during experiment, because the required time for one cycle is 1.4 hours. At the same time, specimens UV lamp were turned on during the heating time to simulate sun facing and shadow facing of space crafts. The approximate total exposure time was ten hours.

2.4 3-point Short Beam Shear Tests

Laminated short beam specimens were used to investigate the effect of MWNTs and thin ply on ILSS of the composite material under LEO environment. The specimens were fabricated and tested according to ASTM D2344. The size of the specimen is 36 mm × 12 mm × 6 mm and the stacking sequences are $[0]_{54}$ for normal ply thickness composites (CN, MWNT-CN) and $[0]_{108}$ for thin ply thickness composites (CT, MWNT-CT).

After aged under LEO environment, the specimens were tested under 27°C, -100°C and 100°C respectively to verify the effect of temperature and find out the most severe temperature condition. To make different temperature conditions, the tests were performed in an environmental test chamber. The chamber (Instron 3119-407) can make the temperature to -100°C by evaporating the liquid nitrogen (LN_2) and 100°C by electric heating system. The grips and loading bars of the apparatus were placed inside the environmental chamber and any gaps between them were sealed with an insulating material. For the high and low temperature test, each specimen maintained at 100°C and -100°C for 30 minutes to make an equilibrium. After 30 minute, the 3-point short beam shear tests were performed.

For each test, 5 specimens were tested to obtain the ILSS property.

3. RESULTS AND DISCUSSION

3.1 Base-line interlamina shear strength

Fig. 3 shows the results of base-line ILSS of each material system. The ILSS was improved by adding the MWNT and making the thin ply. The increment rates were 15.6%, 7.7% and 19.7% for CT, MWNT-CN and MWNT-CT respectively.

The effect of MWNT on ILSS of CFRP composite was verified by comparing the CN and CT with MWNT-CN and MWNT-CT. For the both of CN and CT, ILSS were slightly improved by adding functionalized MWNT. The normal-ply composite improved 7.7% and the thin-ply composite improved 3.5% in ILSS. The main mechanism of increase on ILSS by adding MWNT is the bridging effect of MWNT which restricts the generation and propagation of cracks [18]. The fracture surface was observed by using the scanning electron microscope (SEM) to verify the bridging mechanism. Fig. 4 shows the failure surface of no MWNT added composite and MWNT added composite. As shown in Fig. 4(a), for the no MWNT added composite, it shows clear detachment and clear propagation of cracks at the matrix region. But for the MWNT added composite case in Fig. 4(b), the cracks were restricted when it reached at MWNT rich region and the many new surfaces were generated at the matrix region during crack propagation.

The ILSS was largely improved by making the prepreg with thinner ply. It was improved 15.6% for no MWNT reinforced, and 11.1% for MWNT reinforced composite. Even though it was stacked with same fiber direction, as $[0]_{54}$ for normal ply and $[0]_{108}$ for thin ply, ILSS was different. If the boundaries

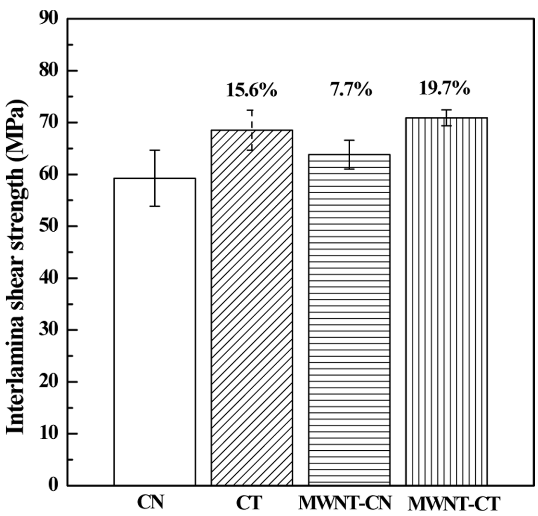
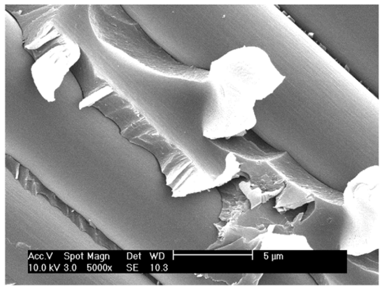


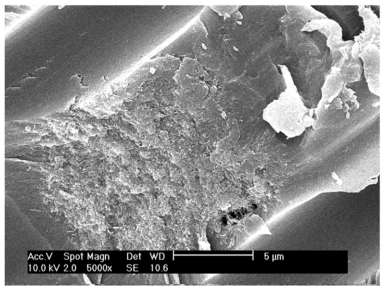
Fig. 3. Base-line ILSS for each material

Table 2. ILSS of each material

Denotation	Interlamina shear strength [MPa]	Standard deviation [%]
CN	59.27	9.1
CT	68.53	5.6
MWNT-CN	63.81	4.3
MWNT-CT	70.92	2.2



(a) No MWNT added composite



(b) MWNT added composite

Fig. 4. Fracture surface of 3-point short beam shear test specimen

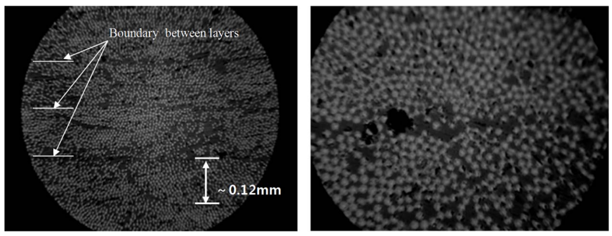
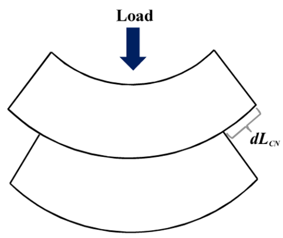
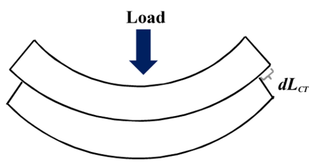


Fig. 5. Cross section composite (x200 and x500)



(a) Normal thickness ply



(b) Thin thickness play

Fig. 6. Schematic diagram of shear strain generation between laminas

between the laminas were obscure, ILSS could not be different. But as shown in Fig. 5, the boundaries between laminas were obvious and it is a resin-rich region. Due to the obvious interface and different ply thickness, the different shear strain and stress were induced by the same applied load. And the strain is proportional to the difference between upper and lower ply. As shown in Fig. 6(a), for the normal ply composite, the difference of length (dL_{CN}) is larger than that of thin ply composite (dL_{CT}). Therefore, much less stress was generated at the thin-ply composite case under same loading condition. It means that thin ply can carry much more loads than normal-ply composite before the shear failure.

3.2 ILSS after simulated LEO exposure

After 20 hours exposure under simulated LEO environment, short beam shear tests were performed. The results are shown in Fig. 7. The degradation rates were -7.5%, -11.0%, -19.9% and -14.4% for CN, CT, MWNT-CN and MWNT-CT respectively. All the ILSS were decreased after LEO exposure, especially, the ILSS of MWNT added composite (MWNT-CN, MWNT-CT) were degraded much more than that of no MWNT added composite (CN, CT).

MWNT is known as good material to improve ILSS of CFRP and it is verified in the previous chapter. And it is good to improve tensile strength and to reduce total mass loss by protecting the polymer matrix from AO [26]. However, in the case of ILSS, MWNT had negative effect under LEO environment even though it had positive effect at normal condition. It was induced by the difference of major affected constituent of LEO. In contrast with tensile property, the major factor was not the atomic oxygen but the thermal cycle in ILSS. The atomic oxygen generates recession and cracks on the exposed surface. But it is not severe for the short beam specimen because the shear failure occurred inside the specimen and its thickness is relatively larger than that of tensile specimen. On the other hand, thermal cycle affected inner part of specimen. The interfacial debonding and micro-cracks were

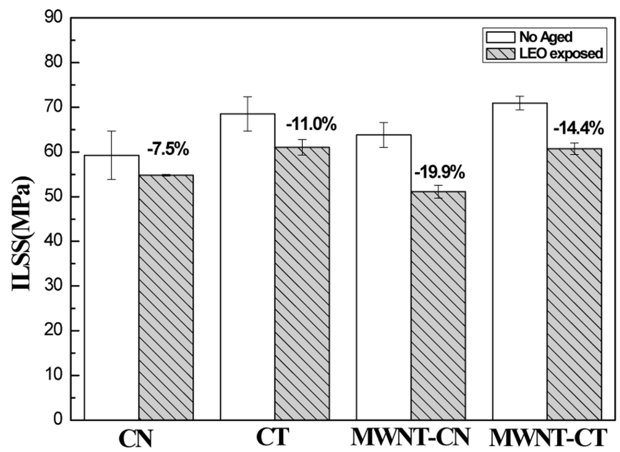
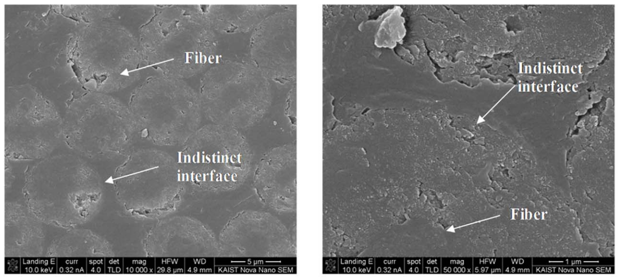
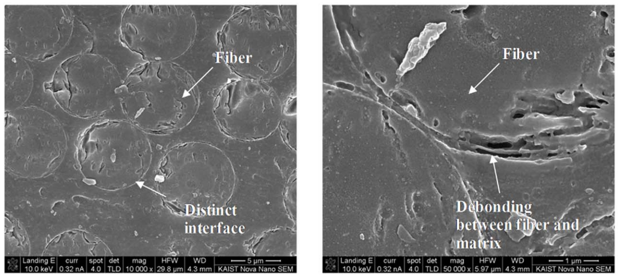


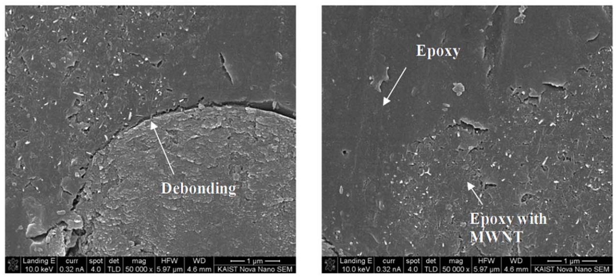
Fig. 7. ILSS before and after LEO exposure



(a) Cross section of no aged composites (X 10,000 and X 50,000)



(b) Cross section of LEO exposed composites (X 10,000 and X 50,000)



(c) Cross section of LEO exposed MWNT added composites (X 50,000)

Fig. 8. Cross section of short beam specimen (interface between fiber and matrix)

generated due to the different coefficient of thermal expansion (CTE) between MWNT and matrix.

The cross section of the aged specimens was observed by using SEM image. Fig. 8 shows the cross section of each material before and after exposure to LEO. For all specimens, the interface between the fiber and the matrix was indistinct before exposed to LEO because the fiber and matrix were well bonded. But the interface became distinct after exposure to simulated LEO condition due to the generation of debonding between matrix and fiber as shown in Fig. 8(b). Large range of the thermal cycles induced the large thermal strain at the fiber-matrix interfaces and it made the failure of interfacial bonding because fiber and matrix have different CTE. Fig. 8(c) shows the cross section of MWNT-added composite after simulated LEO exposure. In the matrix region, it divided into two parts, MWNT-rich region and resin-rich region. At the resin-rich region, there were no micro-cracks but many micro-cracks were observed at the MWNT-rich region. Similar with debonding at the interface between fiber and matrix, thermal strains were induced by thermal cycling between MWNT and matrix. Because of the difference of CTE of MWNT and matrix, thermal stresses were induced and micro-cracks were generated at the MWNT rich region. Due to these micro-cracks, MWNT reinforced composite showed much higher degradation rate than no MWNT reinforced one.

3.3 ILSS after LEO exposure with different testing temperature

The spacecrafts operate under different temperature condition induced by the sun-facing and shadow-facing which cause the thermal cycle. To verify the characteristics of composites under different temperature condition, short beam shear tests were performed at -100°C and 100°C by using the environment chamber after LEO aging.

Fig. 9 shows the results of ILSS according to the different testing temperatures: 27°C, -100°C and 100°C. The characteristics of ILSS under different temperature were extremely different. After LEO simulated, all the specimens showed lower ILSS values than the baseline except at -100°C testing condition. At the low temperature condition, degraded ILSS due to LEO exposure was largely recovered. It was due to the matrix toughening effect under low temperature [18]. Especially, the thin ply composite shows much larger recovery rate at the both MWNT reinforced and no MWNT added composite. Even though the composite was degraded by LEO environment, the ILSS of the thin ply composite is improved in the low temperature condition. In contrast, the ILSS was largely decreased at high temperature and the difference according to material system was relieved. It was due to the rubbery mode of epoxy. The glass transition temperature of epoxy was lower than the 100°C, therefore the epoxy acts as rubbery mode.

To verify the results, typical stress-displacement curve at different environmental conditions was shown in Fig. 10. At the room temperature, the stiffness of the specimen is almost same before and after LEO exposed condition. But the first load drop was occurred earlier when it was exposed to LEO environment. And both LEO-aged and no aged composites showed small load drops. At -100°C, the stiffness of the specimens are increased for both the normal ply composites and the thin ply composites. Also they carried much more loads than others but large amount of loads were dropped rapidly. This means the generation of sudden large interfacial delamination due to the brittleness of epoxy under low temperature. In contrast with MWNT-CT, the first load drop is observed at the early state at the MWNT CN. Due to the early load drop, the ILSS recovery of the normal ply composites under low temperature is smaller than that of the thin ply composites. No distinct load drops were observed at high temperature and the load carrying capacity was largely lowered.

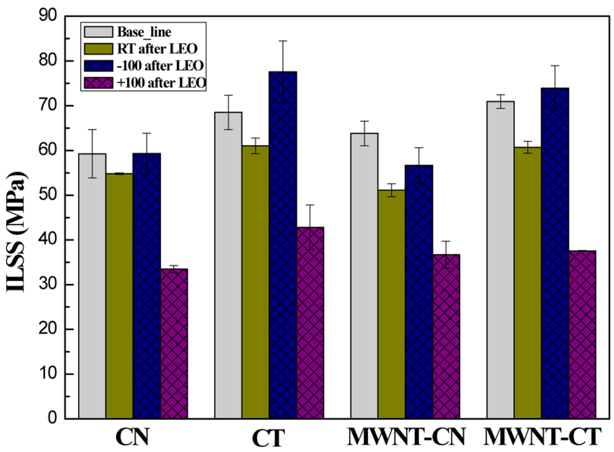
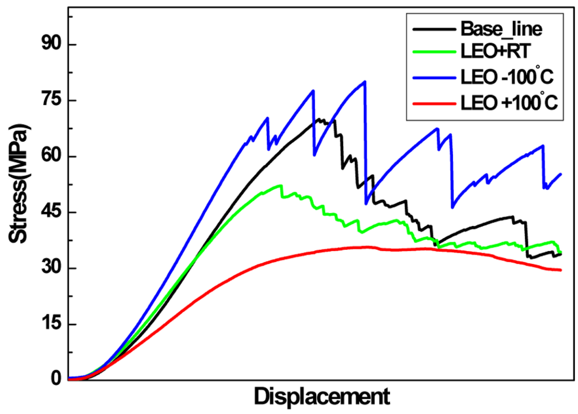
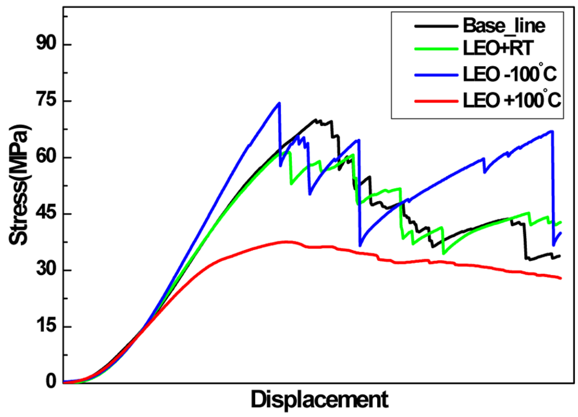


Fig. 9. ILSS under different aging condition and test tempera-



(a) MWNT-CN



(b) MWNT-CT

Fig. 10. Typical stress-displacement curves

4. CONCLUSION

In this study, thin ply composites and MWNT reinforced composites were suggested as space application materials to improve the ILSS which is one of the matrix dominant properties. To verify the changes of the ILSS under the LEO space environment, accelerated ground simulation tests were performed for conventional composites (no MWNT reinforced and normal ply thickness), thin ply composites (no MWNT reinforced but thin ply thickness), MWNT added normal ply thickness composites and MWNT added thin ply thickness composites. After the aging experiment, short beam shear tests were performed at three different temperature conditions (room temperature, 100°C and -100°C).

The ILSS was improved by applying thin ply thickness and adding MWTN to CFRP under room condition. Especially, the thin ply showed much higher improvement of ILSS than MWNT-added one. And the degradation rate after LEO exposure was much higher when MWNT was added to CFRP as filler. Because many micro-cracks were generated at the MWNT rich region due to the CTE difference between MWNT and epoxy. The degraded ILSS by LEO exposure was highly recovered under low temperature (-100°C) due to the matrix toughening effect but extremely decreased under high temperature (100°C) due to the transition to the rubbery mode of epoxy.

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