SPACE ENVIRONMENT CHARACTERISTICS OF MWNT/EPOXY COMPOSITES

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ABSTRACT

Multi-walled carbon nanotube (MWNT)/epoxy composites were fabricated with different nanotube weight percent (wt.%) concentrations. Ultra-sonication and homogenization were simultaneously used to uniformly disperse MWNTs into the epoxy. The MWNT/epoxy composites were tested in simulated low earth orbit (LEO) environment. Effects of MWNTs content on space environment characteristics of the nanocomposites were studied herein. The LEO space environment simulation was characterized by high vacuum (~10^{-5} Torr), ultraviolet (UV) radiation (<200nm wavelength), temperature cycling (-70°C~100°C), and atomic oxygen atmosphere (AO flux of ~10^{16} atoms/cm^2·s and kinetic energy of ~0.04 eV). The tensile properties as well as mass loss of the nanocomposites with various nanotube concentrations, exposed to the simulated LEO environment, were investigated. The surface morphology of MWNT/epoxy nanocomposites under space environmental effects was observed by scanning electron magnetoscope (SEM).

KEY WORDS: Nanocomposites, Space Environment, Atomic Oxygen

1. INTRODUCTION

Polymers and polymer matrix composite (PMC) materials are widely applied to space structures and systems on account of their extraordinary optical, thermal, electrical and mechanical characteristics. Space environment, especially in low earth orbit (LEO) where a large number of spacecrafts including Space Shuttle and International Space Station operate, is however very hazardous toward the polymers and PMCs. The LEO space environment constituents composed of high vacuum, ultraviolet (UV) radiation, thermal cycles, atomic oxygen (AO), charged particles, electromagnetic radiation, micrometeoroids, and man-made debris significantly degrade the characteristics of polymeric materials and PMCs used in the spacecrafts. Not only reliable understanding of destructive space environment effects but development of polymers and polymer based composite materials in space application for next generation are thus of great concern.

Recently carbon nanotubes (CNTs) are of great interest in various fields of application such as field emission displays, memory devices, electrodes, hydrogen storages, reinforcement of composites, etc. because of their excellent mechanical and electromagnetic characteristics. Due to the outstanding characteristics of CNTs and the ability to be dispersed evenly and uniformly in polymeric matrices, the use of carbon nanotube reinforced polymer matrix nanocomposites are regarded herein as a new means to overcome the disadvantage of the polymeric materials and polymer-based composites against such a destructive LEO space environment in space application.

In this paper, the LEO space environment simulation and fabrication of multi-walled carbon nanotube (MWNT)/epoxy nanocomposites with dispersion methods is briefly introduced. And, the synergistic LEO simulation effects on MWNT/epoxy composites in accordance with MWNTs content as well as the mechanisms of changes in properties are investigated and described.

2. LEO SPACE ENVIRONMENT SIMULATION

A LEO space environment facility capable of simulating the characteristics of LEO environment constituents such as high vacuum, UV radiation, thermal cycling, and atomic oxygen atmosphere was designed and manufactured to study the characteristics and degradation mechanisms of the polymer matrix composite materials under LEO space environment. Figure 1 presents a schematic of the simulation facility.

2.1 High Vacuum Vacuum near space structures in LEO is about 10^{-6}~10^{-7} Torr. Such high vacuum in LEO induces outgassing of polymers and PMCs and consequently results in surface contamination and changes of dimension and characteristics of the materials. A main vacuum chamber of a size of 500ϕ×400H(mm) was manufactured to imitate the LEO vacuum condition. The pumping system composed of both rotary pump and diffusion pump for low and high vacuums, respectively, was used to produce the chamber pressure on the order of 10^{-6} Torr at a gas extraction rate of 10 L/s. Vacuum gauge system consists an ion senor measuring within a range of 1×10^{-3}~10^{-10} Torr and a convectron sensor of 760~1×10^{-3} Torr. A vacuum gauge controller was used to control the vacuum.

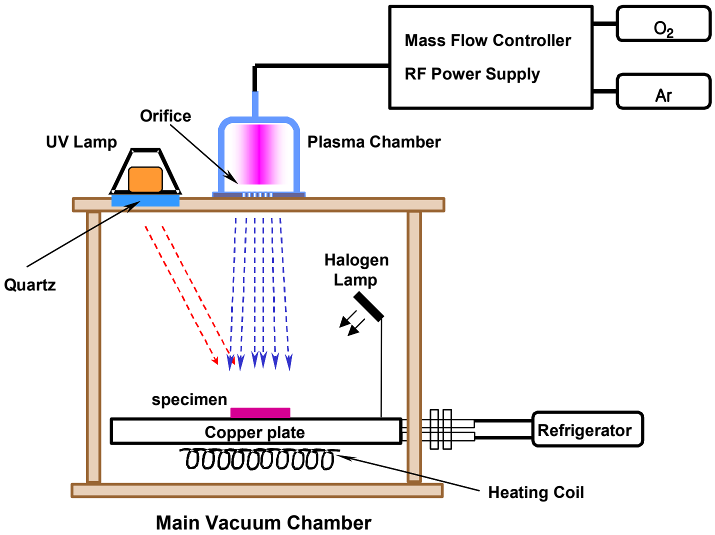


Fig. 1. LEO space environment simulation facility.

2.2 UV radiation UV radiation of the wavelength of 100~200 nm is the primary electromagnetic radiation component in LEO environment [1]. Thermo-optical and mechanical properties are likely to be degraded through UV radiation exposure. The UV radiation source in the LEO simulation facility was manufactured using UV lamp carrying its wavelength of less than 200nm. As shown in Fig. 1, the UV lamp was placed on exterior of the chamber to avoid the excessive outgassing phenomenon on the source when placing inside the chamber. A quartz plate was placed between the UV radiation lamp and chamber so that UV radiation reaches inside the chamber without any loss of wavelength.

2.3 Thermal Cycling Thermal cycling of +150°C to –150°C takes place on between sun-facing and shadow-facing of spacecraft operating in LEO [2]. The thermal cycling induces a mismatch in the coefficients of thermal expansion (CTE's) of the matrix and fibers and hence initiates microcracks in matrix of composite materials, which results in degradation of mechanical properties of the composite materials.

The sun-facing temperature was simulated using a halogen lamp set inside the chamber, and the shadow facing temperature using a refrigerator circulating reusable coolant through a pipe mostly placed below a copper plate. The copper plate on which the nanocomposite specimens were placed is inside the main chamber as shown in Fig. 1. A temperature sensor (T/C) was set on the copper plate to be aware of the temperature of specimen. The maximum and minimum operating temperatures for the thermal cycling simulation were 100°C and –70°C, respectively. Temperature increases at a rate of approximately 5°C/min and decreases approximately 3~4°C/min; and a thermal cycle (-70°C $\rightarrow$ +100°C $\rightarrow$ -70°C) takes about 90 minutes.

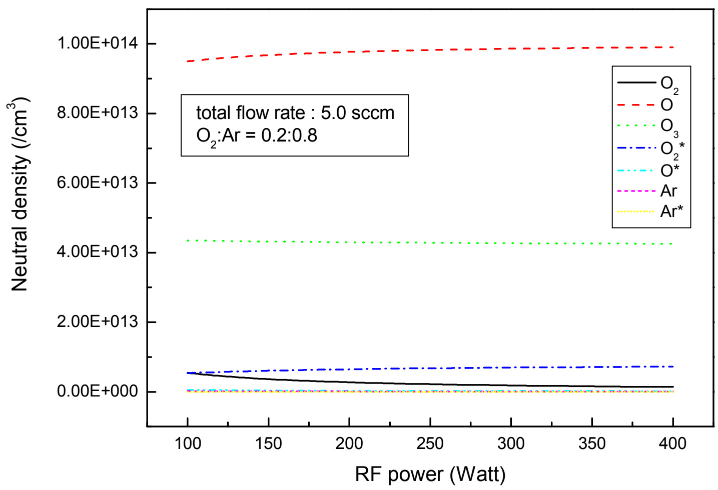


Fig. 2. Densities of neutral species vs. RF power.

2.4 AO Atmosphere In LEO, a major neutral constituent that is very hazardous toward polymers is AO. Surface erosion, mass loss, degradation in mechanical, thermal and optical properties, and changes in chemical compositions of polymers can be resulted through the collision with AO [1]. At an altitude of about 300 km, the densities of AO during maximum and minimum solar activities are approximately 2×10^9 and 8×10^9 atoms/cm^3, respectively. If a spacecraft orbits at the altitude, it travels at a velocity of 8 km/s and would be encountered with AO particles with kinetic energy of about 5 eV and the nominal AO flux range approximately from 10^{14} to 10^{15} atoms/cm^{2}s [3].

LEO AO simulation was generated through weakly ionized remote oxygen plasma using a radio-frequency (RF) plasma source. The plasma source was mainly operated through gas (O_2 and Ar) supply and 600W, 13.56MHz RF power supply. Plasma parameters such as O_2 and Ar gas flow rates, RF power (100-400 watt) and orifice hole size (26.55-191.64 mm^2 of total hole area) were used to determine the maximum AO flux through plasma discharge simulation which was coded based on the rate constants for a restricted set of two body reactions of interest in modeling low-pressure oxygen discharges [4]. Having regard for vacuum condition of the main chamber, the maximum total gas flow rate and orifice hole size were determined as 3.0 sccm and 191.64 mm^2, respectively. The plasma discharge simulation was subsequently performed to estimate the optimum gas composition and RF power, which induce the maximum density of AO for the oxygen plasma. The estimated optimum gas composition of oxygen and argon (O_2:Ar) and RF power were 0.2:0.8 and 200W, respectively, and the maximum AO density was approximately 9.77×10^{13} cm^{-3}. Figure 2 shows densities of neutral species in plasma as a function of RF power at a total gas flow rate of 5.0 sccm with the optimum gas composition. The maximum AO flux was then calculated through the equation as follows:

$$\Gamma_N = \frac{1}{4} N \, \upsilon_N^{TH}$$

where Γ_N is flux of neutral species, N is density of neutral species, $\upsilon_N^{TH} = \sqrt{8T_N / \pi M}$ is thermal velocity of neutral species, T_N is temperature of neutral species, and M is mass of neutral species [4]. The estimated temperature of atomic oxygen neutrals in the oxygen plasma was approximately 0.04 eV. The calculated maximum AO flux was thus of approximately 6.05×10^{17} atoms/cm^{2}s.

AO flux encountered upon the specimen in the main chamber, which was placed 341mm below the orifice (Fig. 1), was determined by estimating divergence angle of the AO beam. The estimation of divergence angle was conducted through measuring diameter of AO beam exposed to sample specimen as a function of distance from the orifice. Obtaining the diameters of the beam and orifice, the divergence angle and AO flux encountered upon test specimen were calculated to be approximately 6.27° and 6.14×10^{16} atoms/cm^{2}s, respectively, and kinetic energy of AO was about 0.04 eV. Having regard for the nominal AO flux in LEO (250 km, $\Phi \approx 3\times10^{14}$ atoms/cm^{2}s), it offers a quite suitable accelerated simulation testing of LEO AO environment.

3. EXPERIMENTAL

In this study, the fabrication process of MWNT/epoxy nanocomposites with different nanotube wt.% concentrations is briefly explained and the mass loss and the change of mechanical properties of the MWNT/epoxy nanocomposites under LEO space environment are investigated. The aging period of simulated LEO environment exposure to the nanocomposite specimens was 5 hours and 45 minutes. The AO fluence over the period was about 1.27×10^{21} atoms/cm^2, and 4 thermal cycles were taken during the aging period.

3.1 Materials The MWNTs (>95% purity) used as filler were synthesized by CVD, thermal decomposition of hydrocarbon. The diameter and the length of the MWNT were 10~20 nm and 10~50 μm, respectively, and the TEM image of MWNTs used in this study is shown in Fig. 2. Epoxy of a maximum service temperature of 130°C, used as matrix, was purchased from HK fiber Co. as a copolymer solution composed of acetone, anhydride-type resin and hardener.

In solution process, both ultra-sonication and homogenization were performed on the solution at the same time for 2 hours to produce a uniformly dispersed MWNT/epoxy solution using a homogenizer of a high-speed revolution of more than 10,000 rpm and a sonicator generating ultrasonic waves. Consequently, it was observed that MWNTs' dispersion state in the solution remained for over 24 hours, which proves that the MWNTs were effectively as well as stably dispersed into the epoxy.

In evaporation process, the MWNT/epoxy/acetone/hardener solution obtained through the solution process above was then dried in an oven set at 70°C over 36 hours so that the solvent be evaporated and hardened. Not only to prevent an appearance of re-aggregation of MWNTs in the dried solution but to extract acetone from the solution more efficiently as well, the solution was stirred at regular intervals within first 3 hours after the evaporation process begins. After the evaporation process, the MWNT/Epoxy nanocomposite was finally fabricated through curing the dried solution in the oven. The MWNT/Epoxy nanocomposites of 0.2, 0.5 and 1.0 wt.% concentrations of MWNTs were fabricated and used in this study.

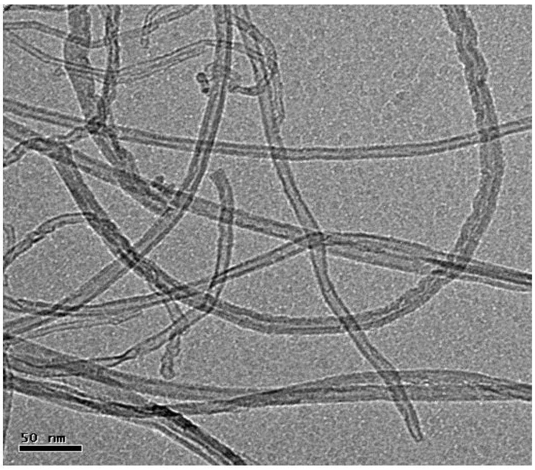


Fig. 3. TEM image of MWNTs used.

3.2 Mass Loss Change of mass occurs on PMC space structures if a spacecraft operates for such a long period in hazardous space environment where polymers degraded by the LEO environmental effects lose their mass through outgassing. The outgassing deforms the structure of spacecraft, causing the contamination and the failure of dimensional stability. Thus, it is strongly recommended that the materials highly resistant to the space environmental effects must be chosen for space applications.

The nanocomposite specimens for mass loss test, the dimension of which is 5×5×2 mm, were manufactured. Total mass losses (TMLs) of the specimens under synergistic LEO environment effects for 5 hours and 45 minutes of aging period were measured using a super precise scale of accuracy of 10^{-4}g.

3.3 Tensile Properties Study of mechanical properties such as tensile stiffness and strength of the polymers and PMCs degraded by space environmental effects is strongly required for their space applications because the space environment characteristics are directly associated with the damage of structures in space. Thus, change of mechanical properties of the MWNT/epoxy nanocomposites after a certain period of exposure to synergistic space environment were investigated herein.

ASTM D638 type V was used as a tension test method to measure the tensile stiffness and strength of the composites. The dog-bone shaped specimens, the dimension of which is 63.5×9.53×1.9 mm, were manufactured as MWNT/epoxy composites with 4 different wt.% MWNT concentrations - 0, 0.2, 0.5 and 1.0 wt.%.

4. RESULTS AND DISCUSSION

4.1 Mass Loss The TMLs of the nanocomposites as well as the pure epoxy, exposed to synergistic LEO environment for the aging period are shown in Fig. 4. The TMLs of MWNT/epoxy composite specimens with 0.2, 0.5 and 1.0 wt.% MWNT concentrations after the synergistic LEO exposure were 8.1%, 7.6% and 7.2%, respectively, whereas the TML of the epoxy was 8.9%. The mass erosion of the epoxy specimen was most severe amongst all the test specimens, as expected. The mass losses of the MWNT/epoxy composites decrease as MWNT wt.% concentration increased. It is believed that a larger percentage of MWNTs dispersed in epoxy blocks AO – the major LEO environment constituent to erode the surface of polymer – more efficiently. From the results of mass loss, it is also predicted that the mechanical properties of the epoxy may be degraded the most after being exposed to the synergistic LEO environment.

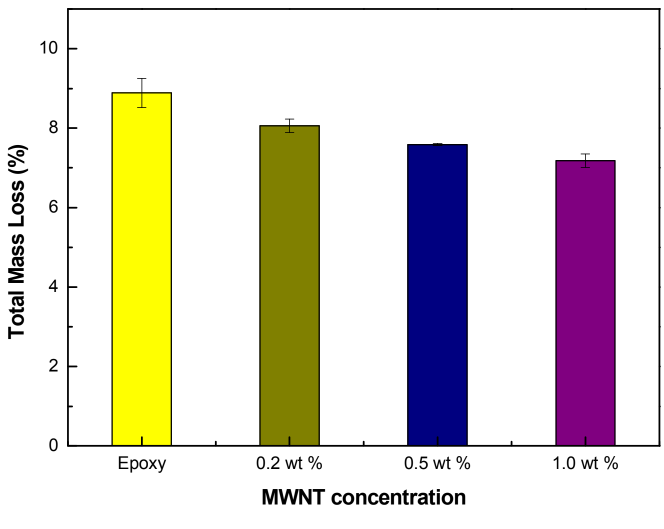


Fig. 4. Total mass loss (TML) vs. MWNT wt.% concentration.

4.2 Tensile Properties Figures 3 and 4 show the tensile stiffness and strength of the MWNT/epoxy composites exposed and unexposed to synergistic LEO environment as a function of MWNT wt.% concentrations. The tensile property of the pure epoxy, whether exposed or unexposed to LEO environment, was improved when an appropriate amount of MWNTs was reinforced.

The both tensile strengths of the MWNT/epoxy composites unexposed and exposed to LEO environment were the maximum values as 72.27 and 72.54MPa, respectively, at 0.5 wt.% MWNT concentration. Relative to the other nanocomposite samples, the strength of the MWNT/epoxy composite with 1.0 wt.% concentration was as exceptionally low as 58.67 and 60.24MPa. It was probably caused by a fact that using a viscous state solution mixed with 1.0 wt.% of MWNTs during the evaporation process, the solvent is hardly evaporated and stirring the solution to remove re-aggregation of MWNTs is not easily performed.

The tensile strengths of nanocomposites slightly increased even with considerable amount of mass loss through the LEO environment effects, except the pure epoxy. It is possibly inferred that a little amount of acetone left in the composites was further extracted under LEO environment through such LEO environment constituents as high vacuum, thermal cycling (high temperature) and UV radiation and induced an increase of the tensile strength of the nanocomposite. On the other hand, the tensile strength of the pure epoxy was slightly decreased after LEO exposure, which leads to an assumption that in case of the pure epoxy, a relatively large amount of mass loss by AO attack primarily affects its tensile properties.

The stiffness of the MWNT/epoxy composites was greater than that of the epoxy regardless of the exposure to LEO environment. The composites had the maximum and minimum stiffness at 0.5 wt.% and 1.0 wt.% MWNT concentrations, respectively. The whole tendency in stiffness is similar to that of strength, except that the stiffness of the MWNT/epoxy composites is slightly decreased after the LEO exposure.

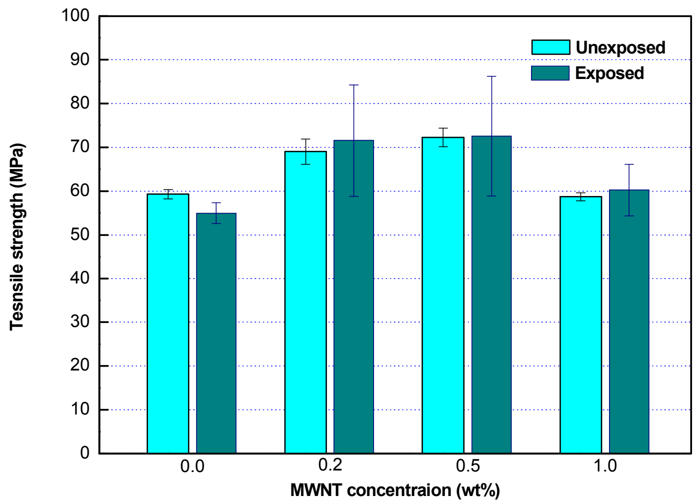


Fig. 5. Tensile strength vs. MWNT wt.% concentration.

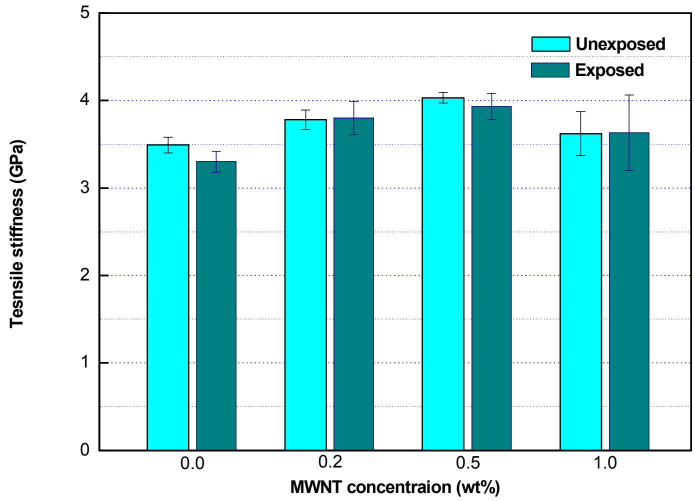
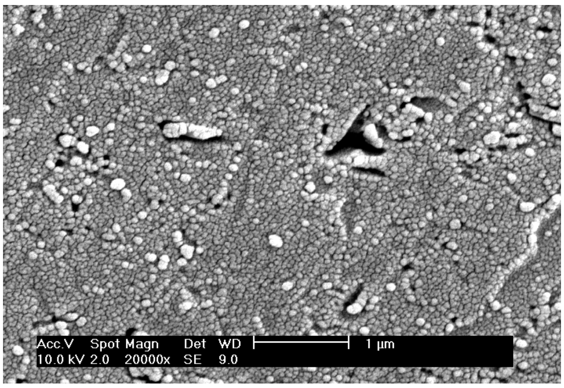
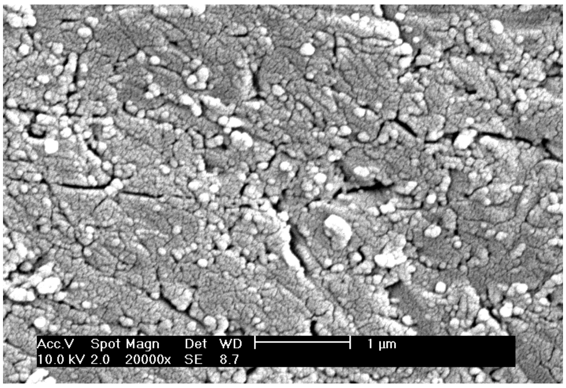


Fig. 6. Tensile stiffness vs. MWNT wt.% concentration.

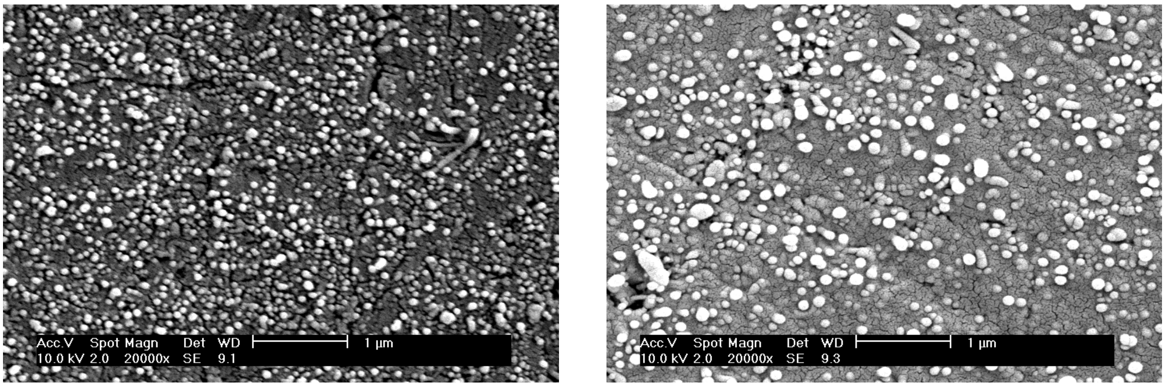
4.2 Surface Morphology Surface morphologies of all the specimens were taken by SEM in order to observe the surface appearance of the exposed and unexposed specimens to LEO environment as shown in Fig. 7. However, the defected surfaces of specimens by synergistic LEO environment were very difficult to be observed because of a large number of MWNTs observed on the surface and an insufficient number of thermal cycling (4 thermal cycles) performed during aging. Thus, the surface morphologies of the pure epoxy and the MWNT/epoxy composite with 0.5 wt.% concentration, shown in Fig. 7, were only selected to display herein.



(a) pure epoxy unexposed



(b) pure epoxy exposed



(c) 0.5 wt.% nanocomposite unexposed (d) 0.5 wt.% nanocomposite exposed

Fig. 7. Surface morphologies of SEM of MWNT/epoxy composites with wt.% concentration, exposed and unexposed to synergistic LEO environment.

Figure 7 shows the surface of 0.5 wt.% MWNT/epoxy composite exposed and unexposed to LEO environment. The MWNTs impregnated in matrix are observed in both LEO exposed and unexposed specimens; however, after the exposure, not only the epoxy but also the MWNTs appeared to be defected or changed in their chemical compositions. Based on the different surface morphologies between exposed and unexposed specimens and the results of tensile properties – the increase and decrease of tensile strengths of MWNT/epoxy composites and pure epoxy, respectively, it suggest that further research, such as the examination on chemical compositions of MWNT exposed to LEO environment through energy dispersive spectroscopy (EDS), is required to understand the correct mechanism of change in tensile properties.

5. CONCLUDING REMARKS

MWNT/epoxy nanocomposites fabricated with 4 different MWNT wt.% concentrations were exposed to LEO space environment simulation and the space environmental characteristics of MWNT/epoxy nanocomposites were investigated in this study.

Mass losses and tensile properties of MWNT-reinforced epoxy composites and pure epoxy, aged in LEO space environment facility, were compared with those of baseline (un-aged) materials. The content of MWNTs reinforced epoxy was inversely proportional to the mass loss caused by LEO effects. The tensile strengths of the MWNT/epoxy composites slightly increased, whereas the stiffness does not significantly affected through LEO exposure.

Further studies on each individual effect of LEO space environment constituents (AO exposure, a large number of thermal cyclings, UV radiation, etc.) not only on MWNT/epoxy nanocomposites but on MWNTs themselves as well are thus suggested to perceive the more reliable understanding of the LEO space environment characteristics MWNT/epoxy nanocomposites and the mechanism of changes in tensile properties.

6. REFERENCES

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