CFRP Composite Behaviour Under Extreme Environment Exposure

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In space filed usually size doesn't matter but weight does, being a critical point in space structure design stage. Carbon fiber reinforced polymer composite materials are already deployed in many space applications, due to their intrinsic characteristics, mainly their high strength/high stiffness to weight ratio and potential for zero or near-zero CTE, coefficient of thermal expansion. The paper presents the results of the study made on advanced composite exposed to extreme conditions comparable to those found on space environment (Low Earth Orbit – LEO <2000 km). The samples were manufactured from CFRP epoxy composite with different thicknesses (1.2 mm, 1.8 mm, 3.7 mm, 7.7 mm) using autoclave technology. The 1.8 mm thickness samples were coated with 50 and respectively 100 µm of Zn using arc thermal spray technique. Specimens were exposed to UV, gamma radiation and thermal cycles. The results of microstructural, morphological analysis and mechanical characterization showed the aging and damage mechanisms developed post exposure in comparison with reference materials.

Keywords: CFRP, autoclave technology, Low Earth Orbit (LEO), UV, radiation, thermal cycle

Today the entire industry suffers from *the low weight syndrome*, continuously aiming for lighter vehicles with better mechanical resistance, lower energy consumption, reduced pollution and reduced manufacturing costs. Composite materials seem to answer these demands and from the three classes of composites, the polymer matrix composites (PMC) are the lightest and very popular due to their low cost and simple fabrication methods. Fibre reinforced polymeric materials are increasingly being used in space industry due to their high strength/high stiffness to weight ratio, potential for zero or near-zero CTE, high corrosion and fatigue resistance. Likewise, giving the curent trend towards Commercial Off-The Shelf (COTS) components, the orbital life of space systems is substanally reduced since these components are not designed for high radiation tolerance.Therefore systems with COTS electronics require enclosures whose mass is determined by substantial shielding, but also structural requirements. To reduce the structural weigth, satellite designers increaselly replace metallic, aluminium materials with composites. Nevertheless, the integration of advanced composite materials in space structures is not an easy task, due to the critical functioning conditions on the launch and in space environment, those conditions depending on altitude, inclination, solar activity, thermal cycles, etc. Low Earth Orbit, LEO is defined by altitudes between 150 and 2000 km, at this altitude structures being subjected to thermal cycles from -70 to 100°C [1], very low pressure, electromagnetic and gamma radiation, UV, exposure to different atomic species and charged particles [2]. Mechanical strength of space structures is critical during launching stage. Once the structure reached the orbit mechanical loads became negligible, but stiffness of the structure is still important for assuring proper dimensional stability under thermal and environmental loads. Gamma rays, cosmic rays, neutrons, electrons and á particles exists both in space and on earth, exposure to high radiation doses can modify or damage different equipment of spaceships. Radiation level depends on orbital inclination and mission duration and the most radiation exposure come from electron/proton radiation and cosmic rays. A significant contribution to the radiation environment in low Earth orbit (LEO) consists of ã-radiation emitted by the atmosphere. These so-called albedo photons are the ultimate products of impacts by high energy cosmic ray particles on the nuclei of atoms in the upper atmosphere [3]. Figure 1 presents the radiation levels according to the domains of activity, structure or equipment [4].

In research conducted by Kumar et al., carbon/epoxy laminates exposed to cyclic exposure of both UV radiation and moisture condensation totaling 1000 h resulted in a 29% decrease in the transverse tensile strength of the material whereas the longitudinal fiber-dominated properties were not affected. UV radiation and condensation operate in a synergistic manner that leads to extensive matrix erosion, matrix microcracking, fiber debonding, fiber loss and void formation. The epoxy rich layer on the specimen surface was completely removed and the underlying carbon fibers were exposed [5]. Homan et. al. have tested the durability of FRP and its bonds subjected to gamma radiation, showing that up to 291 kGy exposure dose, no significant effect was observed on the strength of room-temperature-cured FRP [6]. Egusa et al. [7] studied the effects of glass transition temperature, Tg, of epoxies on the gamma-radiation resistance of their respective glass-epoxy composites. The epoxies had Tg values of 213 and 165°C. The results showed that the

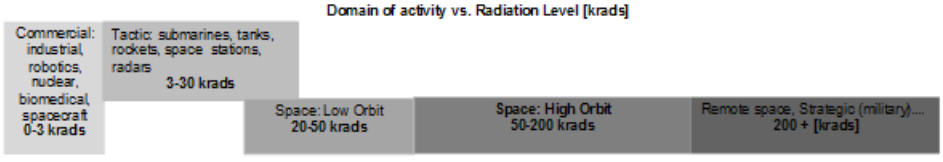

Fig. 1. Field of application with respect to radiation levels [4]

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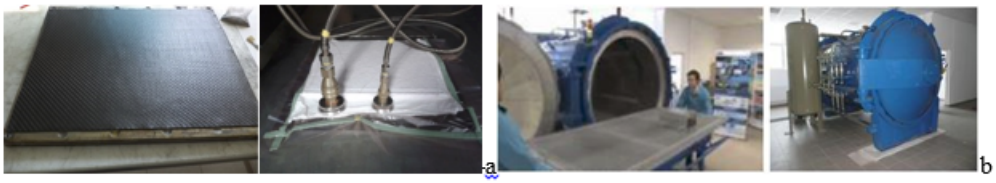


Fig.2. a) Laminates, vacuum bag assembly; b) INCDT COMOTI's autoclave (P_{max}=20 bari; T_{max}=400°C; 6 vacuum lines)

Sample dimension [mm]	Total number of samples	Number of samples exposed to extreme conditions		
		UV [nm]	γ radiation [Gy]	thermal cycling
250 x 25 x 1.2	5	2	-	2
100 x 20 x 1.2	3	-	2	-
100 x 60x 1.8*	4	-	3	-
100 x 60x 1.8**	4	-	3	-
250 x 25 x 3.7	5	1	2	1
250 x 25 x 7.7	5	2	-	2
100 x 25 x 7.7	3	-	2	-

Table 1
DIMENSIONS AND NUMBER OF SAMPLES EXPOSED TO EXTREME CONDITIONS (WHERE * AND ** REFERS TO 50MM RESPECTIVELY 100MM ZN COATED SAMPLES)

strength of the composite short beams with a Tg of 165°C increased with increasing radiation at relatively low doses, below 5 MGy, reaching a value comparable to that of the composite with a Tg of 213°C. Such an increase in strength was not observed in the composite with Tg of 213°C. He suggested that the strength increase for the composite with Tg of 165°C was, at least in part, due to radiationinduced cross-linking in the epoxy network structure. After exposure to doses higher than 5 MGy, identical degradation patterns were observed in both types of composites. In other study Egusa and coworkers [8] reported the effects on the performance of E-glass and T-glass epoxycomposite short beam specimens, of maximum 220 MGy of gamma radiation in air at room temperature. The objective was to determine the influence of fibre type on the durability of FRP. The specimens were tested in three-point bending at -196°C in liquid nitrogen. The observed loss of strength did not depend on the kind of fibre or the type of weave of fabric and the strength loss was due to a change in the ultimate strain of the matrix caused by radiation [8]. Dispennette et al. [9] studied the effects of 546 kGy of gamma radiation on the glass transition temperature (Tg) of postcured and non-postcured carbon-epoxy composite. Only slight changes in Tg were reported. It was also reported that after the radiation, chain scission was the dominant feature of the changes in the post-cured laminates. Cross-linking was reported to be the dominate feature of the changes in the non-post-cured laminates. Giannadakis and Varna [10] studied the effect of thermal ageing of some carbon fiber composite samples and determined their mechanical strength. The samples were exposed to thermal ageing temperature varying between -100 and +100°C. Three sets of samples were used, reference set and two sets with different time intervals, 200 and 400 h. After ageing, each sample was mechanically tested. The main conclusion is that the thermal ageing did not affect the structural integrity of the material in terms of crack density, when the material was subjected to low strain levels (first cracks appear at about the same applied strain).

Experimental part

Composite materials processing

High strength 3k Carbon fiber fabric reinforcement 0/90°, twill2x2, with a nominal weight of 200 g/m^2, and a fiber nominal density of 1.78 g/cm^3, reinforcing M49 Hexcel epoxy matrix (42%) composite, with 0.24 mm cured ply thickness, was used within the preset study. Composite laminates were manufactured using autoclave technology. For the four thicknesses, 1.2 mm, 1.8 mm, 3.7 mm and 7.7 mm, a number of 5, 8, 16 and 33 plies were used. All plies were cut to specific dimensions of 360 x 290 mm (LxW) corresponding to the mould (carbon steel plates) dimensions. Auxiliary materials were used during assembly for cleaning, degreasing the mould, resin excess remove and free passage of volatiles, releasing film (only air and volatiles passage into

the breather layer above), vacuum uniform distribution, bagging, sealing and vacuuming (-0.9 bar). The laminates were cured in the autoclave, at 140°C (3°C/min heating rate), 7 bars during 3 h and then cooled up to 60°C using 4°C/min. cooling rate (fig. 2). Prior to cutting, laminates were NDT and dimensional controlled showing controlled laminate thickness, high compactness, void free structures, due to a proper curing parameter evaluation, good control of resin flow, tested repeatability of the process. Likewise, all consolidated laminates presented 60±1% volume fraction of carbon fiber reinforcement, determined according to ASTM D3171 [11].

All samples under study were cut (by milling) from the cured laminates, the dimensions and numbers of samples allocated for each exposure type are presented in table 1 .

Coted samples

99.9% Zn Ø 1.6 mm wire was deposit on CRFP laminates using arc thermal spaying technique, for protection purpose. Increasing thermal and environment resistance (impact and abrasion resistance, possible surface shielding) were targeted. Sandblasting and degreasing steps were carefully performed during the CFRP substrate preparation, for assuring a *chemico-physical* active surface, with an appropriate roughness. Sandblasting was performed using a Pioneer equipment feed with F30 Electro Corindon White, at 100 mm distance, 4 bars, 6 passages. An AWS400 equipment was used for the metallization process. The electric arc thermal deposition technique was performed at 3.5 bars, 100 mm distance, 20 ÷ 22 V and 150A intensity.

The corresponding code samples and testing configurations are presented below in table 2 (where 1-UV; 2-Gamma radiation and respectively 3-thermal cycling).

	1.2 mm	1.8 mm	3.7 mm	7.7 mm
Reference sample	a ref	Zn ref	b ref	c ref
UV	1a (UV_48h)	-	1c(UV_48h)	1d (UV_48h)
	1b (UV_24h)			1e (UV_24h)
Gamma	2a (γ_200Gy)	2Zn_50μm (γ_10Gy)	2e(γ_200Gy)	2c (γ_200Gy)
	2b (γ_500Gy)	2Zn_100μm (γ_10Gy)	2f (γ_500Gy)	2d (γ_500Gy)
	-	2Zn_50μm (γ_30Gy)	-	-
	-	2Zn_100μm (γ_30Gy)	-	-
	-	2Zn_50μm (γ_200Gy)		-
	-	2Zn_100μm (γ_200Gy)		-
Thermal cycle	3a	-	3c	3d
	3b			3e

Table 2
SAMPLE TESTING CONFIGURATION

Five samples were subjected to *UV radiation* from a VL-220G lamp with two 20W tubes, 254 wavelength and total power of 80W. The five samples mentioned in figure 3, were indexed from 1a to 1e, with respect to their thicknesses (1a and 1b = 1.2 mm; 1c = 3.7 mm; 1d and 1e = 7.7 mm). Exposure distance was 100 mm with different exposure time. Three samples, 1a, 1c and 1e were exposed for 48h (8h/day for 6 days) and two samples, 1b and 1d, for 24h (8h/day for 3 days).

Ten samples were γ irradiated at different doses, using Ce^{137} irradiator (M38-2 model, Gammator 50-G-50B, Radiation Machinery Corporation, SUA) with 0.4 kGy/h. Ce^{137} irradiator provide 0.66 MeV gamma rays. Samples were exposed according to figure 1, for Low Erth Orbit, to a radiation level up to 50krads. Samples 2a, 2c and 2 e were exposed to 200Gy dose whereas 2b, 2d and 2f specimens were exposed to 500 Gy. The 1.8 mm thickness Zn coated samples (2Zn_50μm and 2Zn_100μm) were exposed to 10, 30 and respectively 200 Gy doses.

Samples 3a, 3c and 3d, were exposed to *thermal cycles* in a VOTSCH climatic chamber (CV 4018 model) with 180 L capacity, temperature maximum range of [-40 to +180 °C]., relative humidity range from 10 to 98% only within [10-95 °C]. Each sample was subjected to three cycles of [-40°C/4 h; 100°C/4 h], no humidity, using with a heating/cooling rates of 3°C/min.

Three point bending flexural tests were performed on LFM 30kN *mechanical testing* machine using SR EN ISO14125:2000, environment testing room conditions were measured: temperature 22°C, relative humidity of 45 % and a displacement rate of 2 mm/min. was used. Maximum flexural stress at break (Rm) and flexural strain at break were reported. Note that results of this testing method are sensitive to specimen and loading geometry and strain rate.

Microstructure and morphology analysis were conducted on a Field Emission microscope FE-SEM/FIB/EDS Auriga (Carl Zeiss, Germany), with 1nm resolution at 15kV. EDx analysis performed at 21 kV, alowed semiquantitative chemical determinations. SEM analysis was conducted on both reference and exposed samples.

Results and discussions

SEM analysis aimed to investigate any physical degradation mechanisms resulting from different environmental exposures, by means of microstructure and morphology observations of the composite samples under study. In addition, the degradation chemistry was examined using EDx analysis. The investigations focused mainly on the polymer matrix. Figures 3 present a comparison between the microstructure (SEM images at a 5000 x magnification) of reference and exposed 48 hours to UV 1.2 mm thickeness samples.

No changes on carbon/epoxy laminates with 1.2 to 7.7 mm thicknesses were observed after 24 h exposure to UV, whereas a slight change in color was observed only on the thinner sample 1a (1.2 mm thicness) after 48 h of UV exposure. Likewise 1a sample morphology small degradation can be observed at the fiber-resin interface, degradation which emphasize after 48 h. It is expected that ultraviolet photons absorbed by polymers result in photo-oxidative reactions that alter the chemical structure by molecular chain scission or chain crosslinking when longer exposure will be applied.

Samples exposed to γ radiation did not show any significant degradation. Some changes were observed at

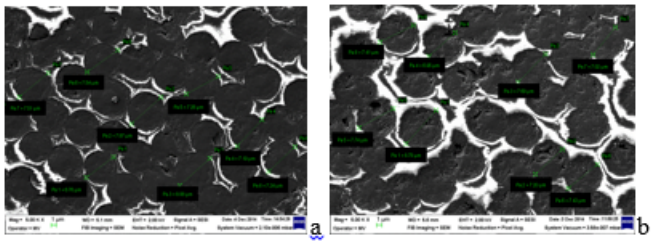


Fig. 3. SEM analysis of a) reference sample a_{ref} of 1.2mm thickness; b) Sample 1a (1.2 mm) after 48 h of UV exposure

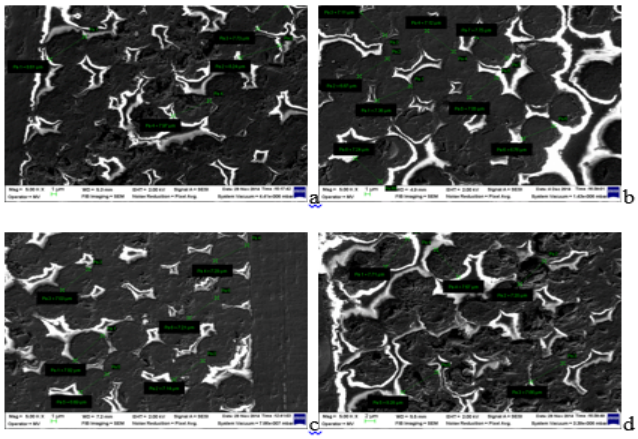
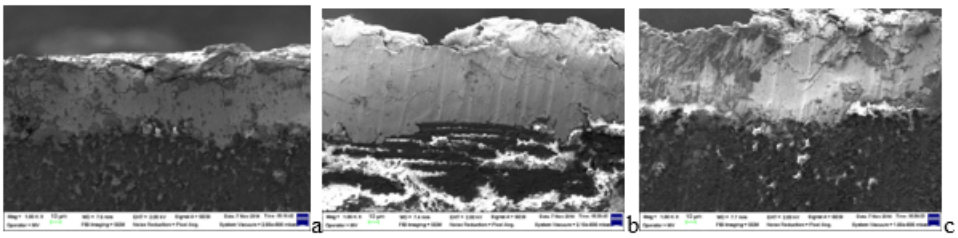


Fig. 4. SEM images of samples subjected to gamma radiation of 200 and 500 Gy. a) Sample 2b (1.2 mm) after 500Gy γ radiation; b) Sample c_{ref} of 7.7 mm thickness; c) Sample 2c (7.7 mm) after 200Gy γ radiation; d) Sample 2d (7.7 mm) after 500Gy γ radiation



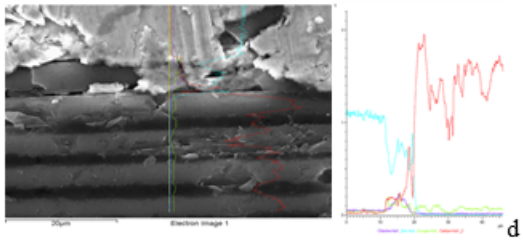


Fig. 5. SEM images of 99.9% Zn 50 µm coated samples a) Zn ref; b) Zn_50µm (γ_30Gy); c) Zn_50µm (γ_200Gy); d) EDx element profile on section area (interface coating/ carbon fibers)

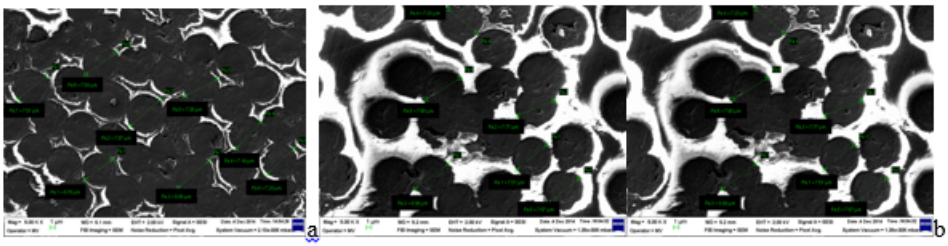


Fig.6. SEM image of sample a) a_{ref} and b) 3a (1.2 mm thicness) after 3 thermal ageing cycles of [-40°C/4 h / 3°C /min./+100°C/4 h]

fiber/matrix interfaces, nevertheless, no cracks or delamination was observed and the integrity of fibers was not affected. Figure 5 shows SEM images of the Zn coted samples morphology. Exposure to 10 to 200 Gy γ radiation doses do not affect the morphological or chemical structure of the coated samples. However, coatings showed a thermal and abrasion good protection, results that will be presented in a future paper.

The effect of short thermal cycling ageing induced some morphological changes of the epoxy matrix, as shown in figure 6. Epoxy resin swelled morphology at carbon fiber/ matrix interface, can be explained by the aabsorption-desorption-reabsorption process during cycling, expulsion of volatiles and residual moisture diffusion in the resin. However, thermal ageing did not affect the structural integrity of the material in terms of cracks, delamination or void appearance. The effect of environment aging on mechanical properties was quantified by conducting static mechanical tests on reference as well as on subjected to UV, thermal cycling or gamma radiation samples. Figure 9 presents the three point flexural tests results of tested laminates.

No major effect was observed on thin samples after short environment exposure. Nevertheless, a slightly increase in strength on 1.2 mm thickness, and a more

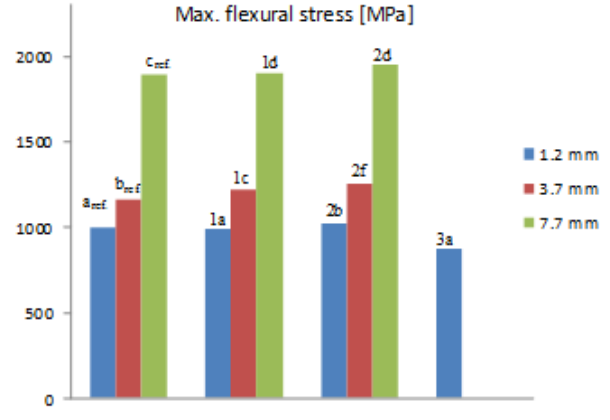


Fig. 7. 3 point flexural tests results on uncoated samples

marked one on thicker (3.7 respectively 7.7 mm) samples, with higher resin content, was observed after exposure to 500 Gy gamma radiation in air at room temperature. Ionizing radiation carries enough energy to liberate electrons from atoms or molecules, thereby ionizing them. Further reaction of ions and electrons lead to formation of free radicals which are highly reactive and eventually they conduct to chemical reactions. The molecular changes occurring in polymers as a result of radiation-induced chemical reactions begins with a chain crosslinking mechanisms in in the epoxy network of the composite structures, effecting an increase in molecular weight and formation of a macroscopic network (polymer solubility decreases with increased radiation dose), followed by chain scission mechanisms effecting a decrease in molecular weight and, thus, substantially changing a polymer materials properties (the rate of dissolution in a given solvent increases). Thus, for longer and harsher environment conditions, it is expected a high decrease of mechanical performances and structural integrity. Likewise, as one can see in figure 7, a loss in both strain and strength was measured on 1.2 mm thickness samples post exposure to 3 thermal cycles [-40°C/ 4h; +100°C/ 4h] using 3°C/h. Thermal aging induced a swollen morphology of the epoxy resin due to residual moisture diffusion during cycling, deboning the polymer chains, affecting the interfacial adhesion with the carbon fibers, and inducing residual stresses by addition mismatch between volumetric expansion of fibers and resin. SEM analyses on fractured samples were not performed in order to observe changes in crack density. On both thicker samples 3.7 mm and 7.7 mm respectively, the UV exposure lead to some increase in flexural strength after 24 and 48 hours, attributable to a higher volume fraction of resin and supplementary curing of the epoxy matrix under UV radiation.

Conclusions

Microscopic analysis of samples exposed to UV, γ radiation and thermal cycling have shown small interface degradation, being more noticeable on thin compared to thicker samples, indicating that volume fraction or

constituents influences the way the structure is affected by environment aging. UV and γ ionization radiation exposures lead to slightly increase in CFR epoxy composite strength, suggesting that, at least in part, is due to radiationinduced cross-linking in the epoxy network structure. On thicker samples with higher volume fraction of resin, additional curing of the epoxy matrix under UV radiation took place. Decrease in both strain and strength was measured on thin samples after thermal cycling aging, caused by residual moisture diffusion during cycling within the resin, deboning the polymer chains, affecting the interfacial adhesion with the carbon fibers, and inducing residual stresses. Nevertheless, results are promising, new polymer systems, coatings, materials, technological solutions will be further analyzed to develop performant FRP composite structures answering to LEO harsh environment and increase their usage in space structures.

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