RESEARCH ACTIVITIES ON NANO-MATERIALS AND ELECTROMAGNETIC PROTECTION OF COMPOSITE AERONAUTICAL STRUCTURES

V. Quero López[1*], F. Sequeiros Murciano[1], F. Cano Pérez[1], K. Molnár[2]

[1]*EADS-CASA Airbus Military, Pº Johnn Lennon s/n Getafe C.P. 28906 Madrid (Spain)*
**Vinas.Quero@military.airbus.com*
[2]*Budapest University of Technology and Economics, Faculty of Mechanical Engineering, Department of Polymer Engineering, Műegyetem rkp. 3-9. H-1111, Budapest, Hungary*

Keywords: Nano-materials, Aeronautical composite Structures, Lightning Protection.

Abstract

Activities within EADS-CASA (Airbus Military) dealing with the use of Nano-materials integrated in Composite Aeronautical Structures to improve the thermal and electrical properties as well as increase the energy dissipation capability produced by a lightning strike are summarized.

Evaluation of mechanical and electrical properties as well as behavior with regard lightning strikes have been performed on laminated samples combined with nano-materials inside the epoxy resin. Besides, rheological and mechanical evaluation has been carried out on Polyacrylonitrile/CNT microfibers which are used as precursor for carbon fibers formation.

1 Introduction

A lightning strike reaches a commercial airplane every 3000 flight hours on average, which is equivalent to one strike by aircraft per year. These values change depending of the atmospheric conditions where the airplane operates. Of all these impacts, approximately 100/year are considered like serious incidents[1].

The massive introduction of composite materials in aircrafts, especially carbon fiber, has presented a revolution with respect to the traditional manufacture of structural elements with metallic materials. On the other hand, the advantages provided by metallic structures in case of a lightning strike, thanks to its high electrical and thermal conductivity, disappear when it is replaced by composite materials like carbon fiber, 1000 times less conductive than aluminum.

As a result, the aircraft is less protected, because lightning creates intense electromagnetic disturbances and currents, which can affect on-board systems (lightning indirect effects) and damage the structure (lightning direct effects)[2].

Airbus military is therefore focused in restoration of the electrical and thermal conductivity, electromagnetic shielding and static discharge drainage features.

The documents and normative paragraphs or sections applicable to provide a secure lightning protection to the aircraft are the following ones:
The civil regulation associated to Large Aeroplanes is the CS-25 (the FAA equivalent regulation exists, FAR 25).
CS 25.581 Lightning protection
CS 25.899 Electrical bonding and protection against lightning and static electricity
CS 25.954 Fuel system lightning protection
CS 25.1316 System Lightning Protection.
For military programs qualification deals with contractual performance which is achieved through compliance with contractual technical specifications.
The compliance approach is based on the process defined in advisory material. Those most relevant for the lightning direct effects protection are: ED-113 (SAE ARP5577)[3], ED-105 (SAE ARP5416)[4], ED-84 (SAE ARP 5412)[5], ED-91 (SAE ARP 5414)[6] and ED-14 (RTCA DO-160)[7].

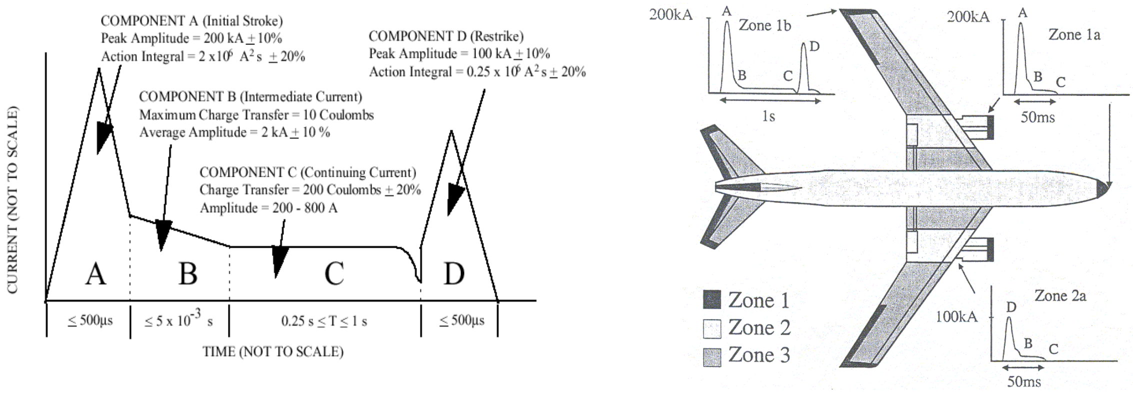


Figure 1: Lightning Test waveforms according to ED-84 [5]

2 First Actuation Step

A solution to the aforementioned problem may be achieved by modifying the matrix component of the composite material in order to increase the electrical and thermal conductivity of the full laminate.

2.1 Carbon Nanotubes (CNT) automatic dispersion

Under the National research projects (2006-2007) and in collaboration with YFLOW[8], LCOE[9] and Carlos III University[10], processes and techniques were prepared to automatically disperse Nano-materials into advanced aeronautical structures in a homogeneous way.

Carbon nanotubes have extraordinary mechanical and chemical properties, but the difficulty of having a proper CNT dispersion, in a given solvent, is a key factor for its industrial use.
The two kinds of commercial Nanotubes ("single walled" and "multi-walled") were evaluated. Although SWCNTs bear better mechanical properties, they are more susceptible to get damaged during dispersion and also their price is too high for current high-scale production. MWCNTs are a good alternative, because their mechanical properties are also

considerably high and their electrical and thermal properties almost reach the properties of SWCNTs.

Dispersion methods based on ultrasonication were developed for preparing nanoparticles solutions in epoxy resin system, sealants and paints to be applied by Electrospinning technique[11].

2.2 CNT Reinforced compounds analysis.

Following the previous development and also under national research projects (2008-2011), in collaboration with FIDAMC[12], YFLOW, LCOE and Carlos III University, the automatic dispersion process has been further developed and electrical, rheological and dispersion analysis of nano-reinforced compounds have been carried out.

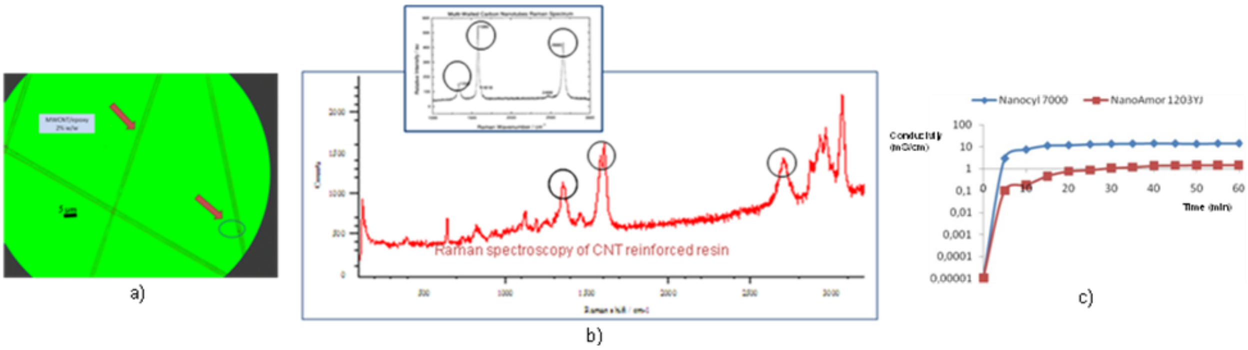


Figure 2: a) electrospinning microfibers. CNT cluster is observed; b) Raman spectrum of electrospinning microfibers with Nanocyl 3100. The peaks in nanoloaded fibers are coincident with the characteristic spectrum of MWCNT; c) Electrical Conductivity of Nanocy 7000 vs Nanoamor 1203 using same dispersion parameters.

2.3 Materials and testing methods.

Based on the dispersion and electrical characterization tests, The Carbon Nano-tubes (CNT) were selected to work with. The CNTs that showed the best results in terms of conductivity/price were Nanocyl 7000, therefore they have been selected for further work.

An automatic system was developed in collaboration with YFLOW for the deposition of epoxy microfibers loaded with carbon nanotubes on carbon fiber laminated panels by electrospinning. The system applies automatically epoxy microfibers with carbon nanotubes on a surface of 2000 mm x 1000 mm and in several laminate positions.

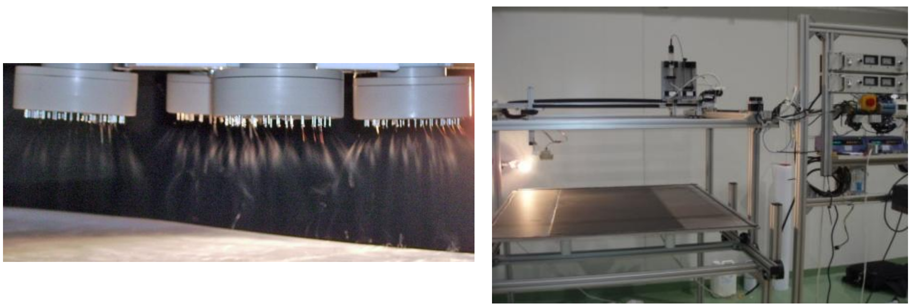


Figure 3: Automatic Application of Carbon nanotubes in laminates by electrospinning.

For lightning and shielding tests, eight flat panels of CFC intermediate modulus tape prepeg cured in autoclave at 180ºC were manufactured. They had several configurations without and with CNT (Nanocyl 7000 – 2%w/w) and several external meshes for lightning protection. The panels' sizes were 1000 x 500 mm and they were cut -out in coupons according to Table 1. For structural test samples, see Table 2.

Nº of Sample	Layup	Coupon Size (mm x mm)	Lightning Protection	Type Test: Shielding ASTM D-4935[[13]] IEC-61000-4-21[[14]]	Type Test: Lightning SAE ARP 5416[[4]]
P-01S	8 plies (±45, 0/90)s	500 x 500	Br Mesh 80 gms	X	X
P-01N				X	X
P-02S			Copper Mesh CM 72 gms	X	X
P-02N				X	
P-04S			Copper Mesh CM 72 gms +CNT	X	X
P-04N				X	X
P-05S	8 plies (±45, 0/90)s + CNT			X	X
P-05N				X	X
P-06S	8 plies (±45, 0/90)s		ECF 195 gms	X	X
P-06N				X	X
P-07S			N/A	X	X
P-07N					X
P-08S	8 plies (±45, 0/90)s + CNT			X	X
P-08N					X
Set P-01A	8 plies (±45, 0/90)s	Ø133.1 Ø133.1 Ø 33	Br Mesh 80 gms	X	
Set P-02A			CM 72 gms	X	
Set P-04A			CM 72 gms + CNT	X	
Set P-05A	8 plies (±45, 0/90)s+ CNT			X	
Set P-06A	8 plies (±45, 0/90)s		ECF 195 gms	X	
Set P-07A			N/A	X	
Set P-08A	8 plies (±45, 0/90)s+ CNT			X	

Table 1: Coupons description for Lightning and Shielding tests

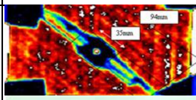
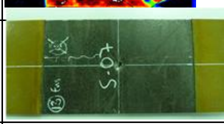
Test Method			Sample Requirement		
Name	Norm Ref	Layup / Thickness	Coupon Size (mm)	Samples/ Test	Total Number
Compression after impact - CAI	AITM 1-0010[[15]]	(45/-45/0/0/90/0)s / 2.5mm	 150 x 100	22	44
Tension after Impact – TAI	I+D-E-026[[16]] AITM 1-0010	(45/-45/0/0/90/0)s / 2.5mm	 290 x 100	18	36
Bending after Impact – BAI	I+D-E-039[[17]]	(45/-45/0/0/90/0)s / 2.5mm	 220 x 100	22	44

Table 2: Coupons description for structural characterization

2.4 Test Results

Simulated lightning test were carried out in collaboration with LCOE according to the applicable regulations [4], [5]. The results are summarizing in the following Figure 4.

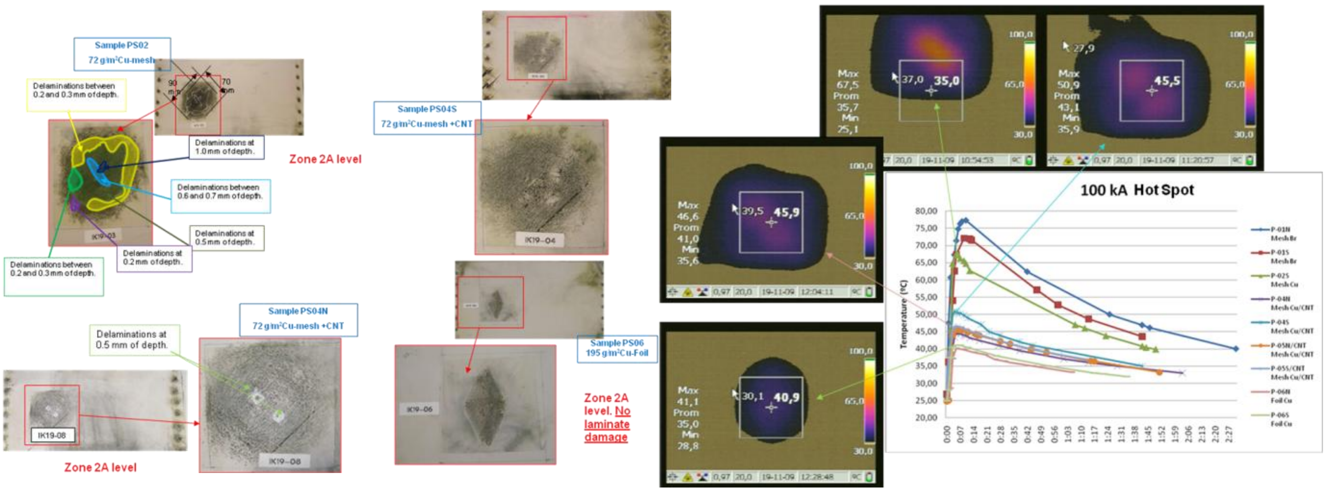


Figure 4: Lightning Test Results &Temperature evolution recorded on the internal face of the sample (hot spot) at Zone 2A. Several Configurations

As shown the previous figures, as a result of the inclusion of CNT within the epoxy resin matrix significant improvement on the lightning protection was noticed.

The allowable of CAI, TAI and BAI were determined by means of the impact and post-impact behavior at failure in compression, in tension and in four points flexure respectively. The tests were carried out taking into account AITM 1-0010, I+D-E-026 and I+D-E-039 as reference.

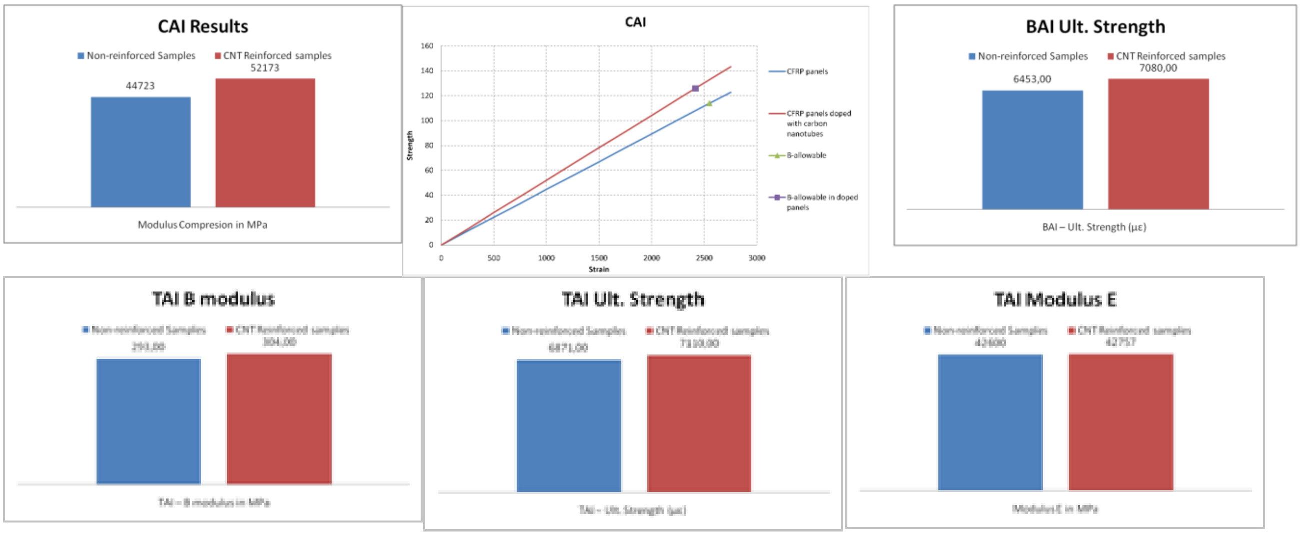


Figure 5: Mechanical Test Results

It is observed that CFRP doped coupons exhibit better compression strength after impact behavior than the reference specimens. Additionally it has been found a higher compression modulus, a slight improvement of the TAI Modulus and a slight improvement in the BAI allowable micro-strains in the CNT reinforced samples.

3 Second Actuation Step

Under the European project Clean Sky GRA (2010-2012) and in collaboration with Budapest University of Technology and Economics [18] the second step to improve the integrity of composite structure against lightning strike have started.

The main objective is embedding CNT into the carbon fiber. Processes to develop microfibers of polyacrylonitrile (PAN) reinforced with CNT have been studied. After carbonization, these PAN-CNT microfibers will be used to create prepreg tapes with epoxy CNT loaded resin.

As in the first step, investigations on Carbon Nanotubes dispersion in epoxy resin have been carried out.
Bayer Baytubes C150 HP MWCNTs (Germany) have been selected based on their mechanical reinforcing potential.
To develop a competitive hybrid composite system, good nanoparticle dispersion has to be achieved. The three-step masterbatch technology [19] has been used for the dispersion of the nanotubes in the epoxy resin. The dispersion tests have been performed on the selected ipox MR 3012 (Hungary) low viscosity epoxy resin with different MWCNT contents.

The masterbatch dispersion method (Figure 6) developed for use with low viscosity resins has been characterized by rheological, particle size measurements (Figure 8) and has been compared to a competitor direct mixing technology (Figure 7). According to the tests the masterbatch mixing technology is suitable for further use, provides good nanoparticle dispersion without MWCNT re-aggregation. The 0,3wt% MWCNT filling has been selected for further use in the project.

Figure 6: The steps of the masterbatch (MB) mixing technology: premixing by overhead stirrer, three roll milling, masterbatch, thinning under vacuum

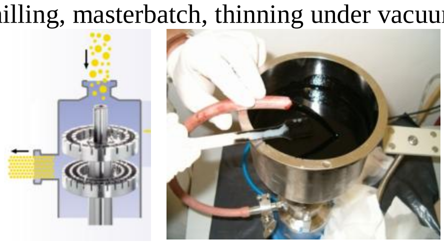


Figure 7: Mixing elements of the IKA Dispax reactor and mixing of the 0.3% weight% MWCNT filled ipox MR 3012 epoxy resin in an IKA MagicLab mixer

To compare the two mixing technologies, fineness of grind and viscosity tests have been performed on the prepared MWCNT filled samples according to EN ISO 1524[20] .

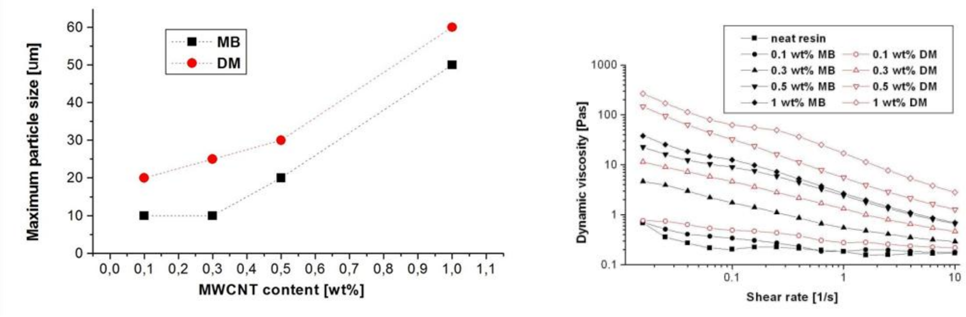


Figure 8: Fineness of grind (maximal particle size) and Viscosity test comparison of MWCNT filled samples prepared by masterbatch technology (MB) and direct mixing (DM)

The dispersion achieved by the used masterbatch technology has been characterized by TEM.

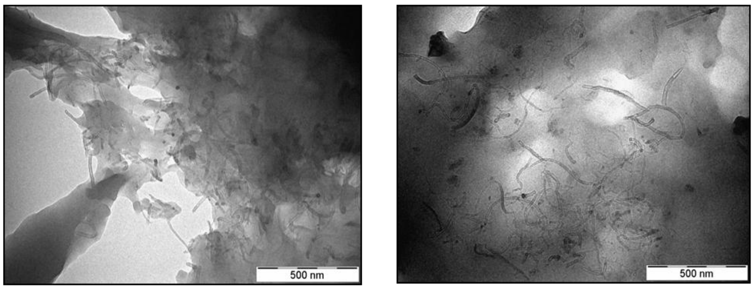


Figure 9: TEM micrographs of the 0.3 wt% MWCNT reinforced MR 3012 epoxy matrix specimens

After that, processes and techniques have been developed to produce polymer nano/microfibers loaded with CNT, which serve as precursors for carbon fibers. The optimal fiber processing parameters and the techniques including CNT dispersion were determined[21].

According to the previous work, the most suitable CNT type was Bayer BT C150 HP MWCNTs and the precursor selected for processing nanofibers was polyacrylonitrile (PAN).

Appropriate dispersion of CNT in PAN solution was achieved by ultrasonication and mechanical mixing. The electrospinning method has been disclosed as an optimal method for precursor fiber formation. The CNT concentration of 2%wt relative to PAN-content was selected.

A new electrospinning device[22] based on the NanoSpider[23] technology was developed, which allows production of nanofiber in a productive and cost-effective way.

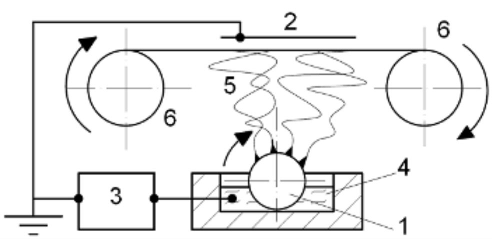


Figure 10: Process for producing nanofibrous tapes by NanoSpider system 1: rotating electrode, 2: grounded electrode (collector), 3: high voltage power supply, 4: electrospinning solution, 5: ventilated fiber formation space, 6: rollers for continuous production

Evaluation of the morphology of precursors before carbonization process was carried in order to verify that the fiber structure is adequate. Determination of the thickness of nanofibrous material was conducted by compression test and SEM analysis (Figure 11). SEM showed no significant difference between the reference PAN nanofibers and the MWCNT loaded ones concerning their uniformity and absence of droplets.

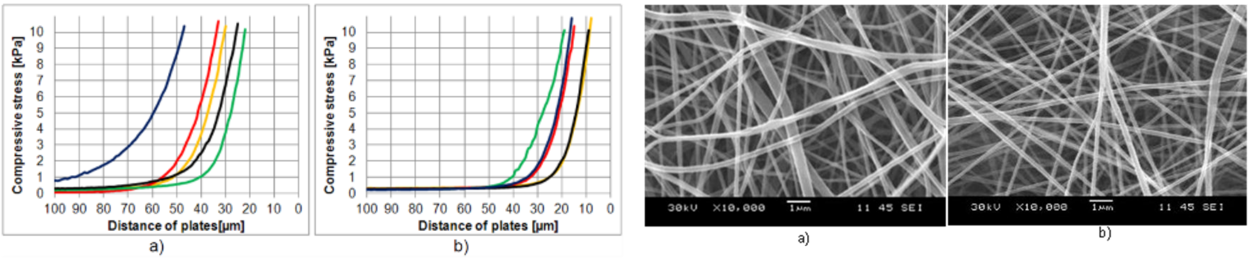


Figure 11: Compression test results on nanofibrous layers a) PAN sample without MWCNT b) PAN sample with 2 wt% MWCNT and SEM micrographs of electrospun PAN nanofibrous mat tapes. a) PAN Nanofibers b) PAN nanofibres with 2wt% MWCNT loading.

Within the next task, the optimization of the thermal treatment of polymer precursor fibers has been studied. Based on DSC and TGA tests, it was fixed the stabilization temperature range between 200 and 240ºC and the total process duration in less than one hour to avoid degradation. Additional stabilization will be carried out continuously in tunnel furnace and in air atmosphere. According to the results, the CNTs make the following stabilization process more controllable and they also increase the electrical conductivity of fibers.

Finally, evaluation of the carbonized nanofibers stabilized under different conditions was attempted. A carbonization above 800 ºC in a laboratory furnace was applied in nitrogen atmosphere. SEM (Figure 12) and AFM micrographs shown that the more stabilization temperature, the less nanofiber diameter with less dispersion as well.

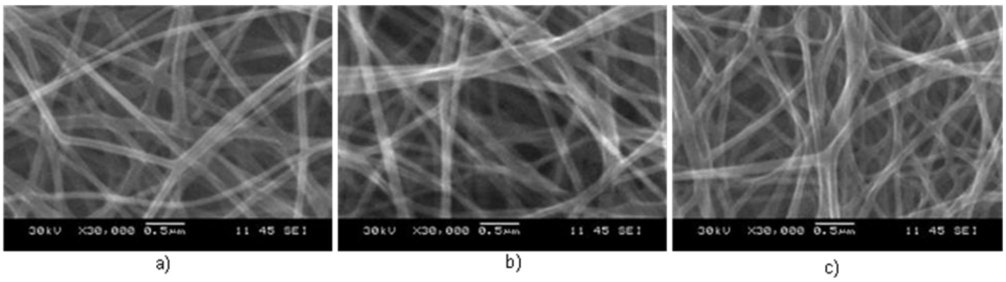


Figure 12: SEM micrographs of carbonized nanofibers at stabilization Temp.: a) 200°C, b) 215°C, c) 230°C

4 Conclusions

Firstly, an automatic system was developed for deposition of epoxy microfibers loaded with CNT on carbon fiber laminates by electrospinning which poses an advantage from the industrialization point of view since the integration with automated tape lay-up production process can be achieved. Additionally an improvement on the behavior against lightning strike was reported on CNT samples with no degradation of mechanical properties.
Secondly, techniques have been developed to produce polyacrylonitrile nano/microfibers loaded with CNT, which serve as precursors for carbon fibers. The optimal fiber processing parameters as stabilization temperature and carbonization parameters were determined. From results it can be concluded that the inclusion of CNT involves a more controllable process.

References

[1] http://www.lightningsafety.com/nlsi_lls/avaition_losses.html

[2] Sequeiros F.; Quero V. *Lightning Protection of Aeronautical composite structures. New Materials* in SETEC 02/07. Madrid, Spain (2007)

[3] ED-113 (SAE ARP5577) - Aircraft Lightning Direct Effects Certification

[4] ED-105 (SAE ARP5416) - Aircraft Lightning Test Methods

[5] ED-84 (SAE ARP 5412) - Aircraft Lightning Environment and test waveform standard

[6] ED-91 (SAE ARP 5414) - Aircraft Lightning Zoning Standard

[7] ED-14 (RTCA DO-160) - Environmental conditions and test procedures for airborne equipment

[8] YFLOW technology: Nanotechnology company http://www.yflow.com/

[9] LCOE: Laboratorio Central Oficial de Electrotecnia. Madrid http://www.f2i2.net/web/lcoe/lcoe_portada.asp

[10] Carlos III University of Madrid: UC3M http://www.uc3m.es/

[11] Barrero Ripoll A., Sequeiros Murciano F., González Loscertales I., Luna Díaz J.M., Lallave Rivas M. *Method for producing nanofibres of epoxy resin for composite laminates of aeronautical structures to improve their electromagnetic characteristics.* EP 2 202 336 A1 (2010) US 2010/0203315 A1

[12] FIDAMC: Fundación para la Investigación, Desarrollo y Aplicación de Materiales Compuestos. Madrid http://www.fidamc.es/

[13] ASTM D-4935: Electromagnetic Shielding Effectiveness.

[14] IEC-61000-4-21: Electromagnetic Shielding Effectiveness

[15] Airbus AITM 1-0010: Fiber Reinforced Plastics. Determination of Compression Strength After Impact.

[16] EADS-CASA I+D-E-026: Tensile test on Carbon Fiber Laminates.

[17] EADS-CASA I+D-E-039: 4-Point flexure Test on Carbon Fiber Laminates.

[18] Budapest University of Technology and Economics: BME http://www.bme.hu

[19] Szebényi G.: Development of fiber and nanoparticle reinforced hybrid composites, PhD thesis, Budapest University of Technology and Economics, Department of Polymer Engineering, 2011.

[20] EN ISO 1524: Paints, varnishes and printing inks -- Determination of fineness of grind.

[21] Kolos M., László M. V., *Development of continuous electrospun precursors for carbon fiber manufacturing. ID-598 of ECCM15 – 15th European Conference on Composite Materials*, Venice, Italy, (2012)

[22] www.elmarco.com

[23] Jirsák O., Sanetrnik F., Lukas D., Kotek V., Martinova L., Chaloupek J: *A method of nanofibers production from a polymer solution using electrostatic spinning and a device for carrying out the method*. U.S. W02005024101 (2005)