Final Publishable Summary Report

Grant Agreement number: CP-IP 213939-1

Project acronym: POCO

Project title: Carbon Nanotube Confinement Strategies to Develop Novel Polymer Matrix Composites

Funding Scheme: FP7-CP-IP

Period covered: 48 months **from** 01/11/2008 **to** 31/10/2012

Name of the scientific representative of the project's co-ordinator, Title and Organisation:

Mr. Borja Coto. Fundación Tekniker

Tel: +34 943206744

Fax: +34 943202757

E-mail: borja.coto@tekniker.es

Project website address: www.poco-project.org

Contents

1. Executive summary

The main objective of the POCO project was to get innovative polymer nanocomposites filled with CNTs in order to obtain materials with tailor made and superior properties. Different S&T strategies were planned to obtain nanocomposites with **CNTs confined, ordered, structured or aligned** into the polymer matrix.The main scientific and technical highlights achieved in the project are the following:

-Growth of CNTs (and graphene) with controlled morphologies by controlling the mixtures of catalysts used as well as low temperature growth on the surface of carbon fibers.

-Successful functionalization of CNTs by different routes and functional groups targeting different host matrices were developed to improve CNTs dispersion and interactions with matrices.

-Successful confinement of functionalized CNTs in the correlating phase of block copolymers as well as nanostructuring of thermosetting matrices were achieved. Moreover, it was found that lamellar nanostructures of selected BCs can be oriented under shear forces and electric fields.

-Different models were setup an/or applied to understand different properties of CNTs and nanocomposites.

-The influence of CNTs as nucleating agents for crystallinity of semicrystalline matrices was succesfully analyzed

-Alignment and positioning of CNTs inside the matrices was obtained by means of the application of electrical and magnetic fields, enhancing the electrical properties of the polymers filled with low CNT content.

-The use of ionic liquids was demonstrated to be an intersting strategy to disperse and functionalize CNTs.

-Testing of toxicology and biocompatibility of the CNTs and nanocomposites developed for biomedical bone implants were performed and the results shown that CNTs are not a problem from the health point of view for this application.

-The influence of the use of CNTs in the processing parameters and final properties o the composites was studied. The main problems for the processing of CFRP epoxy composites containing CNTs were overcomed using different strategies.

-New processing tools were developed for the dispersion of the CNTs and also for the processing of CFRP containing nanoparticles.

-Demonstrator parts with improved electrical and mechanical properties were developed and manufactured for the different applications targeted in project.

2. Description of the project

2.1 Project context

Polymer nanocomposite materials can be made using different type of nano-reinforcements or nanofillers and polymer matrices. Among the different nanofillers, carbon nanotubes (CNT) have been extensively studied because of their exceptional mechanical and electrical properties. Due to these extraordinary properties, great enthusiasm exists among researchers around the world as they explore the immense potential of CNT/polymer nanocomposites. This increase of interest about CNTs has been followed by a reduction in the production prices. This has been possible mainly due to the development of production processes by CNT manufacturing companies like ARKEMA. Price reduction run in parallel with an increase of the CNTs demand, and it is foreseen that this tendency will be accelerated in a near future.

The utilization of CNTs as reinforcement to design novel composites is a quite old idea. However, nowadays their practical and extensive use in commercial materials is still missing. The scientific literature addresses various aspects of nanotube production, functionalization and applications as well as the fabrication and characterization of polymer nanocomposites with various types of carbon nanotubes and dispersion methods.

One of the missing points is a lack of knowledge based approach to achieve the nanostructuring level required to optimize the CNT/polymer nanocomposite performances and an in deep investigation into the polymer/nanotube interphase.

2.2 Project objectives

The main objective of the POCO project is to get innovative polymer nanocomposites filled with CNTs in order to obtain materials with tailor made and superior properties. Therefore, maximum research efforts within POCO will be addressed to the achievement of nanocomposites in which the CNTs are confined, ordered, structured or aligned into the polymer matrix and to obtain new knowledge into the CNT/polymer interfaces.

The final goal is to reach the predicted and expected excellent properties of CNT/polymer nanocomposites in terms of mechanical, electrical, thermal, surface and tribological behaviours. By reaching this ambitious goal, POCO paves the way towards CNT/polymer nanocomposite products for the aerospace, automotive, building and biomedical industries.

The particular scientific and technical objectives of the project are:

- Active chemical **functionalization** of CNTs for their integration in the selected polymeric matrices. The functionalization will be targeted towards the **confinement**, **positioning** and **alignment** of CNTs into the polymer matrix.

- To develop new functionalization methods combining the growth of polymers from the CNTs surface and the physical and supramolecular **interactions** with the polymeric matrix.
- **Growing of CNT** in specific sites of the nanocomposites surfaces using self-assembling concepts based on the modification of matrices with block copolymers. In this way, preferred orientation patterns will be created resulting in ordered nanostructures with novel tailor made properties.
- **Electrical and magnetic alignment and confinement** of carbon nanotubes in different polymeric matrices.
- To analyse **structural properties** and the self-assembling between polymer and nanotubes in order to acquire knowledge about reactivity, stability, ordering and structure of filler anchorage and properties of composites.
- To study, model and characterize the **interfaces** between nanotubes and matrix in the polymer nanocomposites.
- To develop new CNT/polymer nanocomposite products for the aerospace, automotive, building and biomedical industry.

POCO involves the development of different confinement, positioning and alignment strategies of CNTs to develop novel polymer matrix nanocomposites (next generation of nanocomposites) (Figure 2). Several High Performance Polymers have been selected as representatives of thermosetting and thermoplastic materials (epoxy matrices, high temperature thermoplastics, biodegradable thermoplastic, technical polyamides…). This ensures that the output of POCO could be applied in a wide range of applications: automotive, aeronautics, building, aerospace, ship building, biomedicine and optoelectronics. Research activities of this project were focused on four fundamental properties: (i) high strength for structural and mechanical components, (ii) tuneable electrical, (iii) low wear and (iv) surface properties (hydrophobicity, hardness, low friction). Furthermore, multifunctionality of these materials will be an important benefit as the requirements for nanocomposite polymeric materials are quite diverse and demanding.

2.3 The consortium

The ambitious research programme of POCO requires a coordinated multidisciplinary approach by highly specialized and skilled scientist from different disciplines, each one bringing a particular expertise: organic and polymer chemistry, carbon nanotube chemistry, polymer physics, surface and materials science, nanocomposite, modelling, polymer processing, toxicological studies and large scale industrial applications. The POCO consortium is highly complementary, integrating 17 teams from 9 different countries covering the full range of needed skills.

POCO consortium

Nature	Partners
Industries	ARKEMA, EADS, SOLVIONIC, PURAC, INTECO, ACCIONA, CRF
Universities & Research Centers	TEKNIKER, IPF, CIDETEC, CNRS, EMPA, UMONS, EHU, ECNP, UOI, UBA

Fundamental knowledge developed within POCO is oriented to increase competitiveness of European industry. In order to ensure the impact of POCO within different industrial sectors such as aerospace, automotive, building and biomedical, several key industries such as EADS, CRF, ACCIONA and PURAC (respectively employed in the above sectors) participate in the POCO project as end-users. Furthermore, chemical suppliers of CNT, polymers and polymer processing, are also involved in the project (respectively ARKEMA, SOLVIONIC and INTECO).

2.4 Applications addressed in the project

The end-users of the project (ACCIONA, CRF, EADS and PURAC) have established their requirements for final applications following the standards and norms required in their respective sectors:

In aeronautics industry, the use of composite materials in the construction of modern aircrafts is an important application of technological progress. In the POCO project the interest is focused on epoxy resin matrix composite materials. These materials are stable materials and are aiming to replace aluminium and aluminium alloys. This has a significant effect on performance, weight, design and cost.

The interest of EADS, from the aerospace point of view, is double: one oriented to the realization of new epoxy resins composite materials and carbon nanotubes and the second one is to study and realize new coating with increasing mechanical and electrical properties.

In particular from the composite point of view, EADS interest in the POCO project from composite side is focused on the improvement of the mechanical and the FST (fire, smoke & toxicity) properties of CFRPs through the incorporation of carbon nanotubes (CNTs). On the other hand, EADS interest for coating applications aims a further increase of the mechanical strength of coatings (abrasion and erosion resistance) and / or in adding electrical conductivity to the paints. A primer coating containing carbon nanotubes was developed in the POCO project.

Plastics and polymeric composites are also growing in interest in automotive applications due to the possibility of weight reduction and consequently fuel saving. Especially, further application in this area will be useful for new model concept of car like urban cars or electric vehicles.

The main automotive application to be developed in the POCO project, as indicated by CRF is applied to the structural frame in the body closure panel such as bonnets (hoods) or tailgates (hatchbacks).

Construction industry is experiencing a significant increase in the use of composite structures, and calls for accurate and efficient methods capable of modelling and optimizing these structures under different set of conditions. In the last years some works have been developed relating to the analysis of composite beams. One of the most versatile composite processes for manufacturing those structural beams is the pultrusion process, selected to manufacture the POCO final application in the construction field. Structural parts containing carbon nanotubes for pedestrian bridges application were manufactured by ACCIONA.

PURAC develops poly(lactide)s (PLA's) that are used for medical and pharmaceutical applications. Examples of applications are screws and plates for fracture fixation. There is a strong wish from the market for stronger biodegradable materials in order to be able to replace metallic implants by polymeric, biodegradable implants. The incorporation of CNT in PLA may be a useful way to increase the mechanical properties of the material to such a level that polymers may be used in more applications than currently those possible.

3. Description of the main S&T results

The POCO project has lead to significant advances in the field of carbon nanotube nanocomposites from the both scientific and technological points of view. Subsequent sections describe the main results of the project.

3.1 Carbon nanotube growth

ARKEMA has supplied CNTs and masterbatches to the partners in order to perform the research in POCO. Nevertheless, studies on the growth of CNTs were also carried out within the project. Thus, CNTs have been successfully grown on different supports in a controlled way. UBA has succeeded growing CNTs perpendicularly aligned to a substrate with control of the density of CNTs per surface unit, under high temperatures using commercial iron oxide nanoparticles as catalyst. This result allows the growth of CNTs on predetermined patterns. CNTs were successfully grown by CNRS and UBA using different substrates such as Alumina, Epoxy, Glass fibers and carbon fibers between others. The influence of different substrates and catalysts was studied by CNRS leading to a precise control in the morphological characteristics of CNTs allowing to grow CNTs with a narrow distributions of diameters and number of walls (figure 2 right).

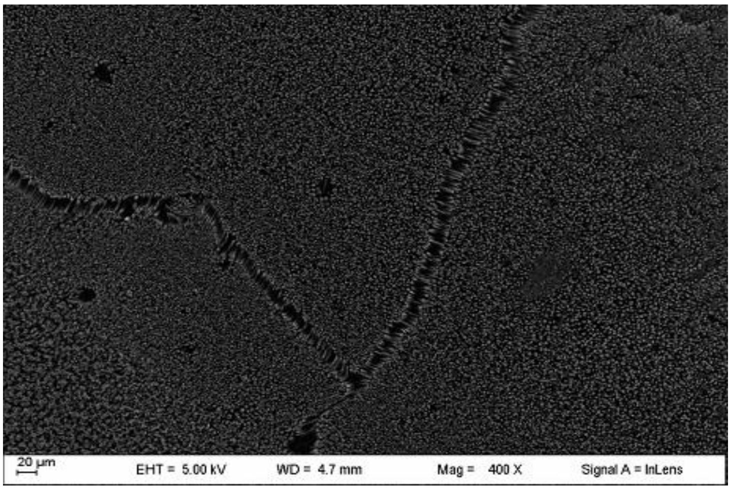

Figure 1. Vertical aligned CNTs after controlled growth.

On the other hand**, UBA** synthesized carbon nanotubes with magnetic properties that were used on magnetic positioning. These nanotubes have nanoparticles of hercynite adhered on their walls and a mean outer diameter of 30 nm, as it is shown in Figure 2. left.

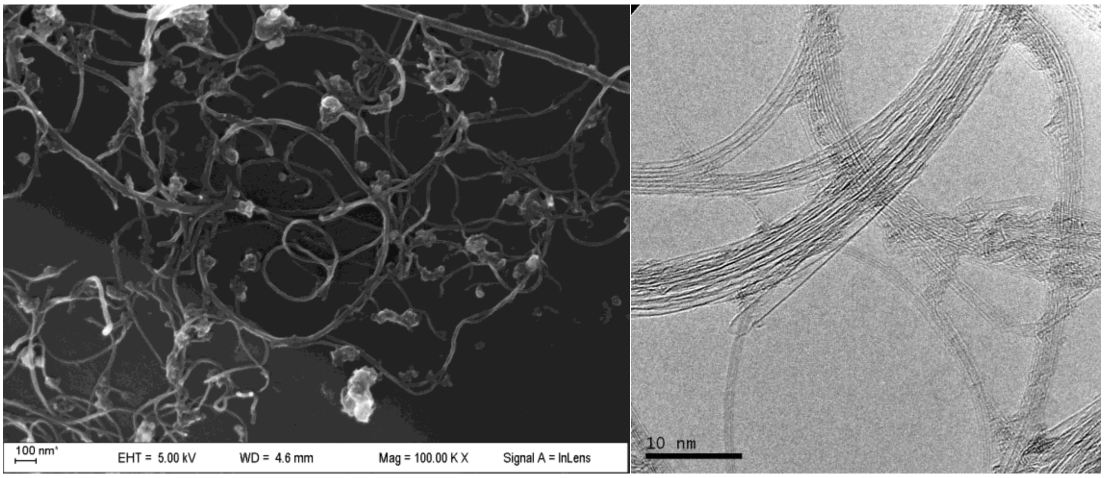

Figure 2. Left: SEM micrograph of carbon nanotubes with small particles of hercynite attached on the walls. Right: TEM images of few walled CNTs grown under controlled conditions

The studies of carbon nanotube growth performed within the POCO project have a real potential for industrial use. In this sense ARKEMA, CNRS, UBA and EHU have applied for 4 different patents to protect the results developed in the project.

3.2 Carbon nanotubes functionalization

The functionalization of carbon nanotubes was used in the project with a twofold objective:

- To enhance the dispersability of the CNTs which tend to agglomerate due to van der Waals interactions.
- To improve the compatibility of the CNTs with the matrices.

CNTs have been successfully functionalized to enhance their dispersion and interfacial behaviour in the matrices. Different functional groups have been added depending on the target matrix while different approaches have been used depending on the type of functionalization:

-Grafting from: polymer growths from the living ends from the MWCNT.
-Grafting to: living chain polymerization of monomers followed by the addition of MWCNT.
-Functionalization by oxidation and further chemisorption of functional groups.
-Functionalization by non-covalent interactions through the modification of polymer chains (physisorption).
-Ionic liquid polymerizations and functionalization via non-covalent interactions.
-Self-assembly of PEO-*b*-PLLA diblock copolymers, lithium chloride (LiCl) and CNTs.

Table 1 summarizes the main functionalizations carried out in the project.

Table 1. Summary of CNT functionalizations

Type of functionalization	**Performed by**	**To be used with**	**Comments**
- [ViEtIm][NTf_2] - [ViEtIm][Br] - [ViHIm][NTf_2]	**CNRS** (in collaboration with **SOLVIONIC**)	Epoxy matrices+ BC	Physical interactions using ionic liquid polymers.
- Pyrene-PLLA - Imidazolium-PLLA -PEO-b-PLLA+LiNa	**UMONS**	PLLA matrices (**PURAC**)	Functionalization via $\pi-\pi$ and cation-π interactions using chemically modified PLLA
-PLLA-b-PDMAEMA	**UMONS**	PLLA matrices (**PURAC**)	Functionalization via charge transfer interactions
-PA6	**CNRS**	PA matrix	Grafting using initiators
-Amine groups	**TEKNIKER**	Epoxy matrices PA	Grafting to oxidized CNTs
-PS	-**UBA** (via oxidation) -**IPF** (TEMPO) -**UOI** (GF and GT)	Epoxidized BC (UBA)	Grafting to and grafting from methods
-PI	**UOI**	PI/PS BC	Grafting to method
-PB	**UOI**	SBS BC	Grafting to method
-P2VP -P4VP	**UOI** **IPF**	PS-b-P4VP BC	Grafting to, polymer TEMPO terminated (anionic).
-PMMA	**UOI**	PS-b-PMMA	Grafting to method

Functionalization has been characterized by different means: assessment of solubility and dispersion in different solvents, TEM, TGA and FTIR.

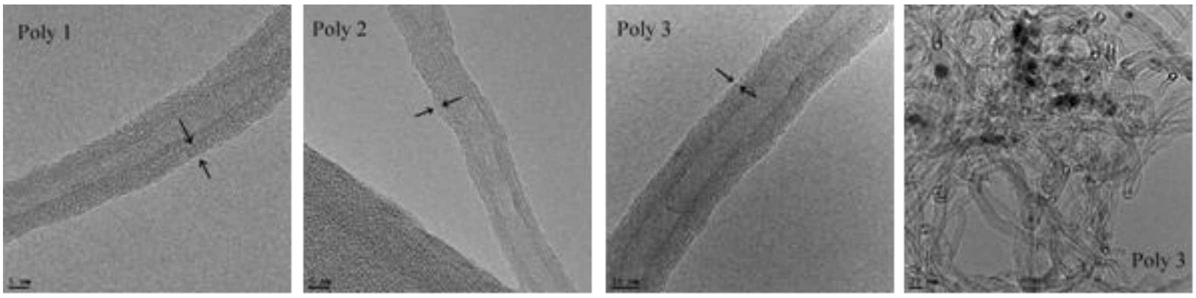

Figure 3. TEM images of MWCNT functionalized by polymerized ionic liquids via *in-situ* method.

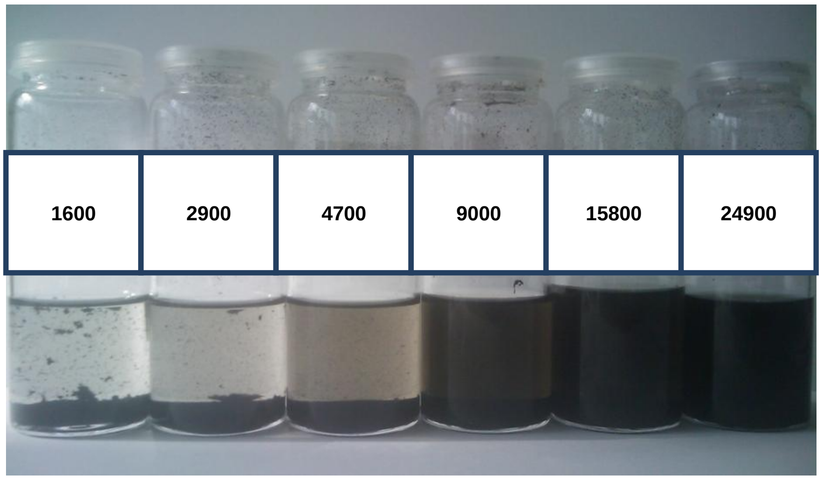

Figure 4. Dispersion of 5 mg of CNTs in $CHCl_3$ with Pyrene-PLLA (corresponding to different molecular weights) after centrifugation.

Together with the experimental analysis of the functionalization performed molecular modelling was employed by Tekniker, in order to understand how the chemical functionalization affects the mechanical properties of the CNTs. It was found that although Young's modulus of CNTs decreases as the degree of functionalization increases, the effect is lower in MWCNTs, so it is possible to functionalize the CNTs moderately without a critical damage of their properties. This modelling approach was also used to perform pull-out simulations to study the interfacial interactions between CNTs and polymer matrices, showing the dependence of the interfacial shear strength on the geometrical parameters of the CNTs as well as the positive effect of functionalization on the interfacial interactions.

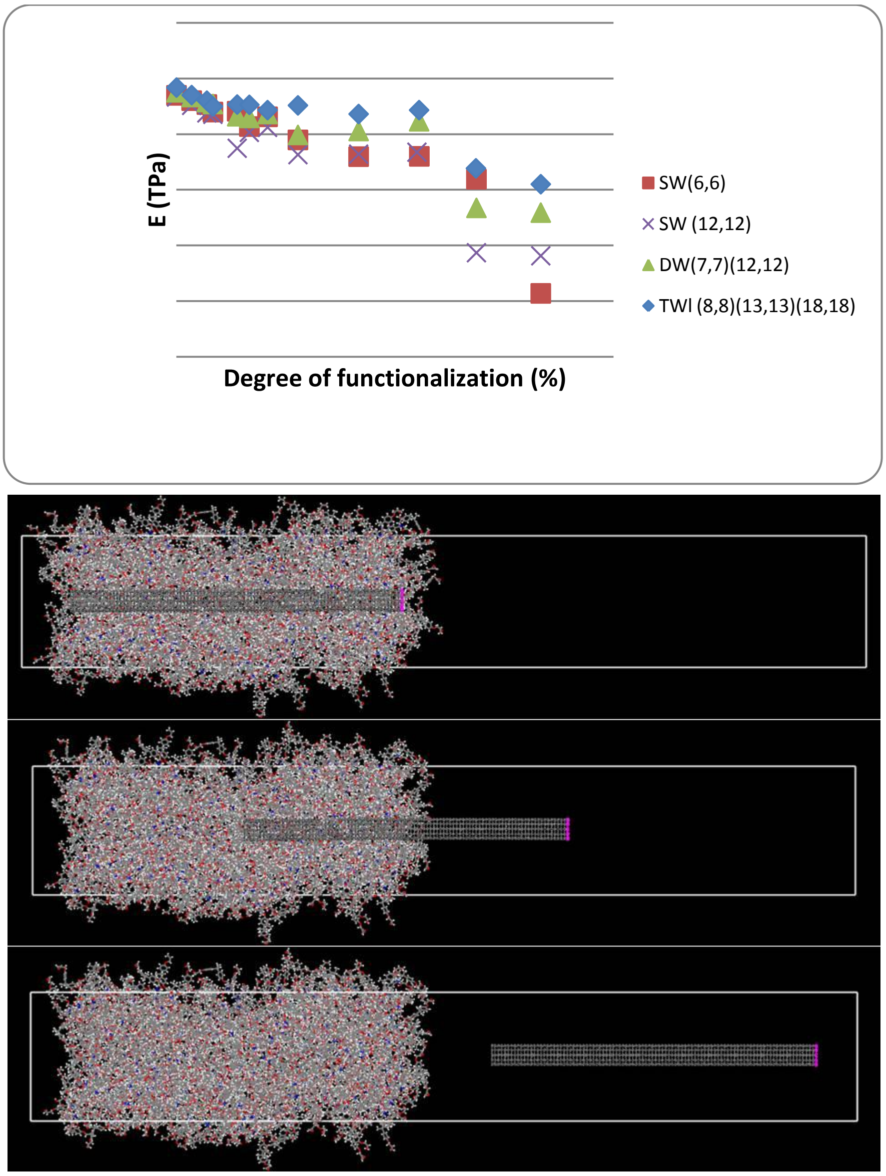

Figure 5. Top: Young's modulus of functianilized CNTs depending on the degree of functionalization. Bottom: snapshots of pull-out simulations.

3.3 Nanostructuration of polymer matrices and confinement

Nanostructuration of polymer matrices by using block copolymers was also developed in the project. Block copolymers (BCs) are an interesting class of nanostructured polymers able to self-assemble into well-defined, periodic nanoscale morphology.

BCs (and in general way polymers) are linear macromolecules composed by a great number of monomeric units covalently linked. Polymers that are chemically different often tend to macrophase separate. Nevertheless, when two polymers chemically different are covalently linked (to form so-called block copolymers), the separation in a macroscopic scale is prevented so the incompatibility between them leads to a separation at local level. So, in the adequate conditions, there occurs the spontaneous formation of a periodic structure (which, taking into account the connectivity between the blocks, is placed at same scale as the radius of gyration of the macromolecules, i.e., on a scale of 10-100 nm), that potentially forms the base for several technologic applications.

Regarding BCs, in the simplest case of two distinct monomers, conventionally termed A and B, linear diblock (AB), triblock (ABA), multiblock or star-block copolymers can be prepared. The phase behavior of such diblock copolymers has been the subject of numerous theoretical and experimental studies over recent decades, and is relatively well understood. Depending on the volume fractions of the building blocks, their molecular weight and the experimental conditions, the intrinsically immiscible blocks can separate in the form of sphere, cylinders, lamellae or gyroids which can acts as templates for sequestering nanoparticles.

The nanostructured morphology that can be obtained for the neat matrix is very important in designing nanostructured composite materials thus taking into account that correspondence between self-assembled matrix morphology and nanoparticle shapes had to be verified. Spherical nanoparticles can be used with every kind of nano-ordered BC structures, while 1-D nanoparticles can be used with lamellar and cylindrical morphologies.

In this project we used BCs as host matrices to sequester CNTs. So, an important aspect to be taken into account is the compatibility between both hydrophobic and hydrophilic materials. Moreover, in general to separate and to solubilize as-synthesized nanotubes, they have to be functionalized. The functionalization could help also the dispersion of the nanoparticles in the polymeric matrix.

In the POCO project different block copolymers were used. **Block copolymers with different molecular characteristics and different polymeric blocks have been synthesized by UOI.** Thus, **UOI** synthesized PS (polystyrene) and PI (polyisoprene) diblock and triblock copolymers, polyisoprene-polymethilmetacrilate (PI-b-PMMA) diblcok copolymers) as well as polystyrene-b-poly(2-vinylpyridine) (PS-b-P2VP) and of PS-b-P4VP sequences. On the other hand, commercial SIS and SBS (polystyrene-b-polybutadiene-b-polystyrene) were also used.

Two different studies were performed in the project using block copolymers:

- Nanostructuring of block copolymers and subsequent confinement of CNTs on selected phases
- Nanostructuring of thermosetting matrices by using block copolymers and subsequent sequestering of CNTs on selected phases.

On the other hand, in the case of semicrystalline matrices the crystallization behaviour of polymer in the presence of CNTs was also analyzed, in order to understand if the crystallinity is acting as a topological constraint for the CNTs.

3.3.1 Confinement of CNTs in block copolymers

Studies of the influence of CNTs on the nanostructuring of the block polymers and the confinementof CNTs in selected phases were performed during the project by different partners.

ECNP worked with SIS and SBS commercial block copolymer matrices using different CNT functionalizations as COOH-CNTs (CNRS), PS-CNTs, PI-CNTs, PB-CNTs (UOI), F-CNTs (ECNP) and pristine Graphistrengh (Arkema). They obtained that PS-CNTs lead (generally) to big agglomerates, PI-CNT to small agglomerates, while for the other functionalized CNTs no agglomeration is observed. The nanostructuration of the matrix is maintained with the addition of the CNTs as observed by AFM and SAXS. However, the confinement of the CNTs in one block of the copolymer has not been clearly observed but partial confinement in phases corresponding to their functionalizations was obtained in some cases for PB-CNTs in SBS and PI- CNTs in SIS. On the other hand, UOI obtained good dispersions of the PI-CNTs in SIS block copolymers synthetized in the laboratory. In this case the selective confinement of the CNTs was not achieved as the sizes of the domains are smaller than the CNTs but preferential attachment of the CNTs to the corresponding phase was found (figure 6).

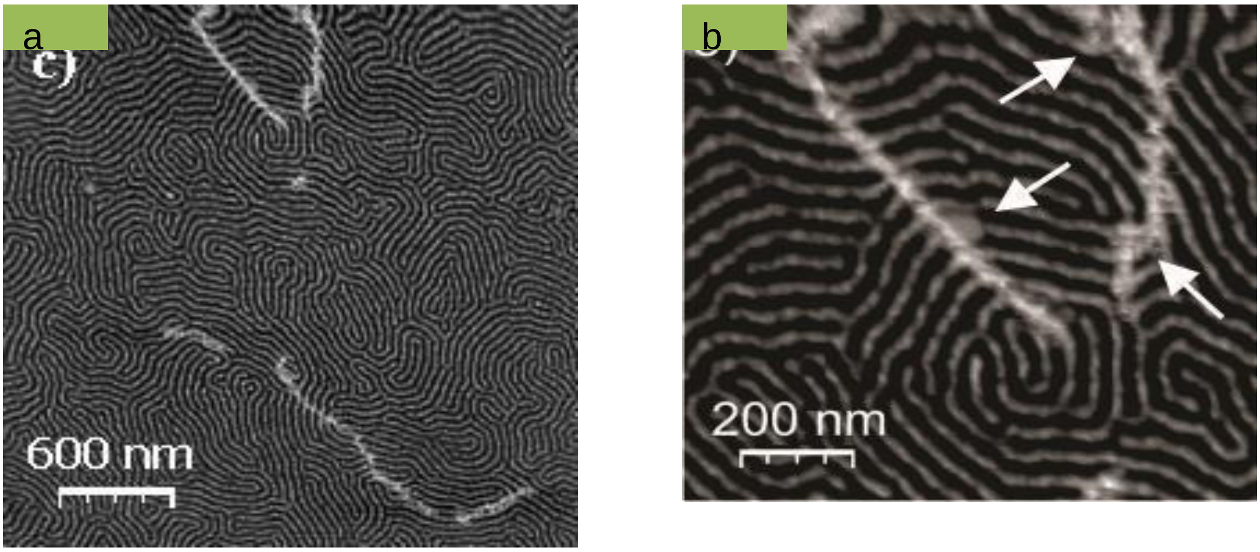

Figure 6. Attachment of functionalized CNTs to preferential phases of nanostructured BCs.

IPF in collaboration with **UOI** worked in the confinement of CNTs on PS-b-P4VP. SAXS and TEM measurements were performed to characterize the systems. Results obtained with cleaned CNTs does not show confinement effect. Nevertheless, **successful sequestering of functionalized CNTs in the correlating phase of BC was achieved as shown in figure 7.**

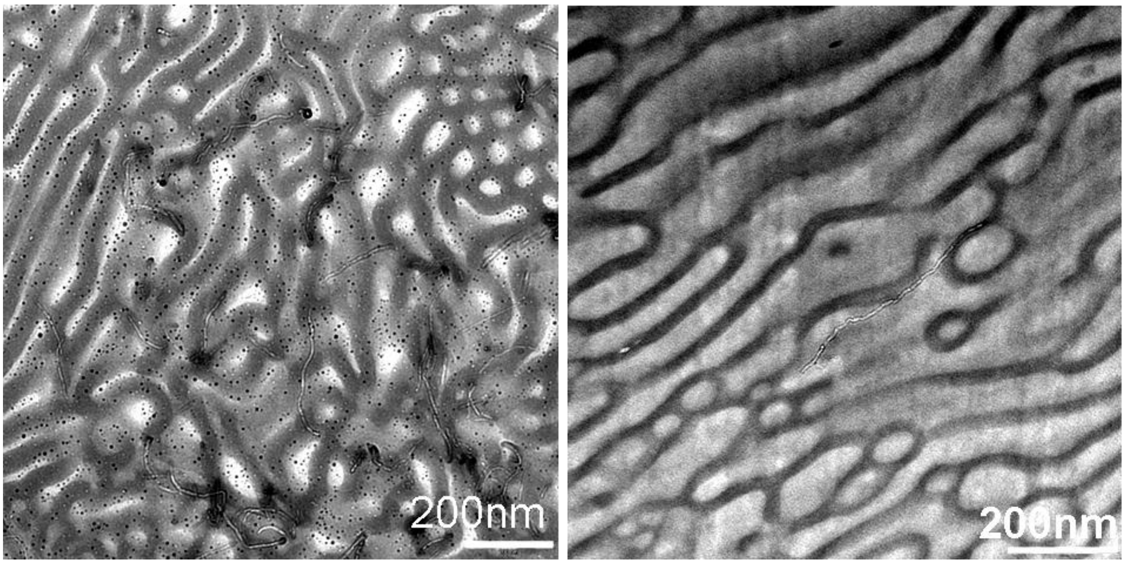

Figure 7. Confinement of CNTs in BCP PS-b-P4VP (P4VP phase is indicated in black (iodine staining)). Left : CNT-g-P2VP; right : CNT-g-PS

On the other hand, CIDETEC studied the synthesis of new block copolymers, where one of the blocks consists of a polymeric ionic liquid (PIL). The PIL block obtained by the quaternization of PS-b-P2VP and the subsequent anion exchange to obtain different PIL blocks: PS-b-poly(ViEtPy^{+}Br^{-}), PS-b-poly(ViEtPy^{+}(CF$_3$SO$_2$)$_2$N^{-}) and PS-b-poly(ViEtPy^{+}(CF$_3$(CF$_2$)$_3$SO$_3^{-}$) which lead to different phase morphologies as shown in figure 8. These PIL BC were used for subsequent nanostructuration of the epoxy matrix.

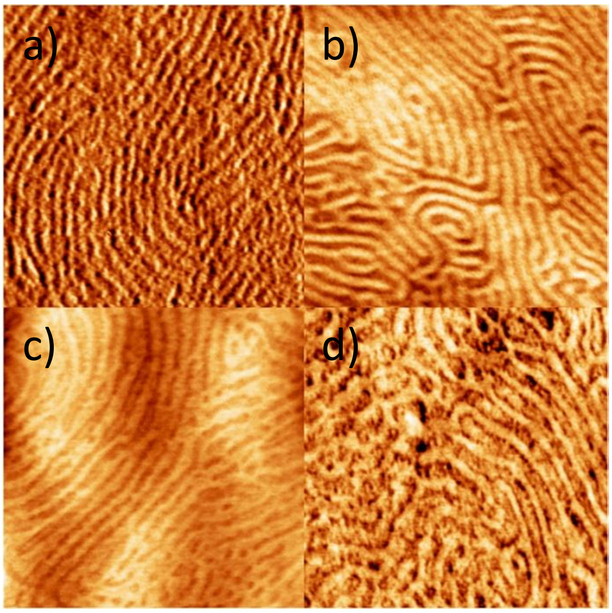

Figure 8. AFM images of phase for (a) PS-b-P2VP (top) , (b) PS-b-poly(ViEtPy^{+}Br^{-}), (c) PS-b-poly(ViEtPy^{+}(CF$_3$SO$_2$)$_2$N^{-}) and (d) PS-b-poly(ViEtPy^{+}(CF$_3$(CF$_2$)$_3$SO$_3^{-}$))

3.3.2 Nanostructuring of thermosetting matrices and confinement of CNTs

Thermosetting matrices (epoxy and unsaturated polyester, UP) containing several contents of block copolymers (epoxidized SBS and PI-b-PMMA for the epoxy matrix and PEO-PPO-PEO for UP) and filled with different weight percentages of carbon nanotubes (CNT) were produced to analyze the confinement of CNT in the nanodomains and the mechanical properties of composites.

Thermosetting systems modified with several amounts of block copolymers and different types of CNT were analyzed.

Epoxy coatings modified with epoxidized SBS, nanostructuring of the matrix was achieved for mixtures containing at least 10 wt% of BC. The confinement of COOH-MWCNT is not achieved, though the use of the BC improves the dispersion of a-MWCNT.

Regarding epoxy/PI-b-PMMA systems, an enhanced dispersion of CNT was achieved by functionalizing CNT with PI chains and the addition of block copolymer, which lead to an increase of the reinforcing effect. The addition of around 1.5 wt% of pure PI to the samples increased the confinement effect (figure 9).

On the other hand, for UP resin nanostructured with PEO-PPO-PEO block copolymer and reinforced with MWCNT, the dispersion of those in the matrix is improved when compared to that in the matrix without BC.

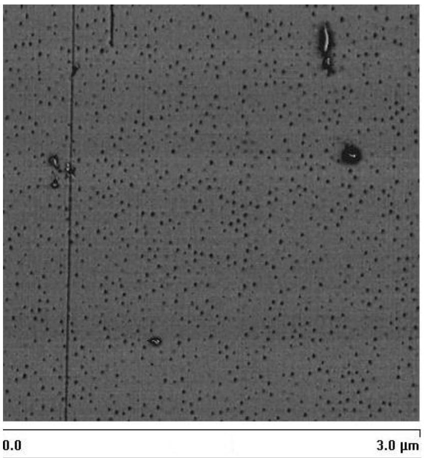

Figure 9. TM-AFM images of epoxy/10 wt% PI-b-PMMA/ 0.05 wt% of PI-g-CNT/ 1.5 wt% PI. Favorable interaction between the grafted polymer and one segment of the block copolymer enables sequestering of the CNT in the preferred domain constituted by that segment.

3.3.3 Crystallinity of semicrystalline matrices and confinement

In order to obtain nanostructured CNT-thermoplastic composites with tailor made properties it is challenging to determine the mechanisms of polymer chain confinement in presence of carbon nanotubes. Both bulk amorphous and rigid amorphous phases of semicrystalline polymers were analysed in PLLA that was chosen as a model polymer for crystallization studies in thermoplastic/MWCNT composites. The effect of carbon nanotube concentration affected the degree of dispersion greatly and hence all kinetics parameters of PLLA crystallization and the morphology

were found to be affected. The confinement of the polymer chains by the tubes leaded to a restrain in chain mobility affecting the glass transition and aging behaviour of PLLA. Thus,
increasing nanotube concentration up to 3 wt. %, the time required for complexion of crystallization was linearly reduced (from 5 min for the pure PLLA to 1.8 min for its 3 wt. % composite).

Results showed that physical aging rate is reduced with the addition of carbon nanotubes, especially at a concentration of 1.25-2.5 wt. %, suggesting that MWCNT restrict the ability of polymer chains to reach a more thermodynamic equilibrium state. During the aging process, all the compositions reflect a continuous embrittlement indicating that some kind of micro-structural reorganization is taking place within the polymer. The proposed relaxation model in which the amount of polymer/nanotube interfaces dominated the overall physical aging rate provides a general understanding of the relaxation mechanism in carbon nanotube-based polymer nanocomposites.

Stereocomplexation can occur blending polylactide enantiomers of opposite configuration and preferably when an equimolar proportion of repeat units is used. There are thermal and mechanical advantages in having these crystals since they melt at higher temperature and present higher stiffness than homocrystals.
The stereocomplex crystallization between two polylactides of high molecular mass, PDLA and PLLA was observed. It was observed that homocrystallization exceeds sterecomplexation within the entire range of compositions, being the enthalpies of stereocomplex the highest for 50/50 blends.
The addition of low contents of MWCNTs to 50/50 blends enhanced the overall crystallinity. However, with high contents of MWCNTs a poor dispersion leads to the formation of agglomerates hindering the crystallization. Furthermore, it has been found that the addition of MWCNTs was not enough for full stereocomplexation; therefore, once again annealing was required. The results suggested that the addition of MWCNTs helps the stereocomplexation, since it was achieved with a less aggressive annealing (at 180 ºC for 4 h).

3.4 Alignment and positioning

Different strategies were planned and developed in the project to align and position the CNTs inside the selected matrices, in order to improve the electrical and surface properties of the nanocomposites. The results obtained are described in the following subsections.

3.4.1 Positioning and alignment using ionic liquids

Ionic liquids (IL) were used in the project as a horizontal strategy that involved several different approaches:

- Functionalization of CNt with polymeric IL (as shown in the table 1 in previous functionalization section)

- Nanostructuring and confinement in BC with a IL block (as shown in the confinement in BC section)
- IL for dispersion and positioning of the CNTs in polymeric matrices

PIL-functionalized-CNTs were used in high temperature thermoplastic (HTTP) PEI matrix. The dispersion state and the morphology of the resulting PEI/MWCNT composite films were characterized by TEM. The TEM micrographs in figure 6 show the distribution of the nanotubes in the polymer matrix at 1 wt % CNT loading. While the samples contain agglomerated CNTs, the funcionalization helped to enhance the disperision whn compared to pristine CNTs. Moreover, TEM analysis reveals an interesting feature of the morphology of the PEI/ MWCNT-PIL sample. In figure 10(c), it is observed that CNTs are aligned. The direction of the cutting traces of the diamond knife is indicated. Clearly, the diamond knife did not align the CNTs during the TEM specimen preparation. Self-organizing alignment of CNTs in a thermoplastic polymer arising from solvent-polymer interactions was achieved.

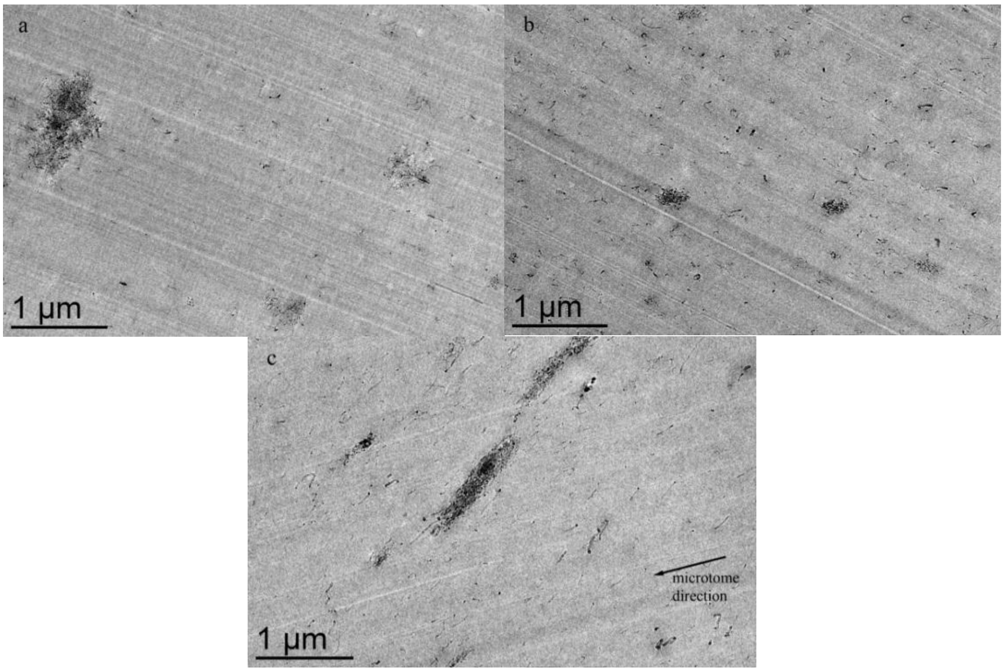

Figure 10. TEM micrographs of PEI/MWCNT composite films at a 1 wt % loading of (a) pristine MWCNT, (b) oxidized MWCNT and (c) MWCNT-PIL.

On the other hand a collaborative effort by SOLVIONIC, CIDETEC, CNRS, IPF and EHU was done to perform a selection of the IL taking into account properties such as the ability to be polymerized, the ability to form stable gels when MWCNTs are added to the IL, and their compatibility with the polymeric matrices (epoxy and semicrystalline)**. Imidazolium based IL were found to be the best candidates.** The use of these polymeric liquids followed by polymerization leads to stable dispersions of the CNTs (figure 11). Moreover, the IL containing CNTs were found to be compatible with the epoxy matrices. On the other hand, final steps of processing lead to porous materials not useful for structural applications. Nevertheless, the results obtained are useful to be applied in other polymeric matrices. In these sense, further use and research is planned by SOLVIONIC through subsequent development of this strategy.

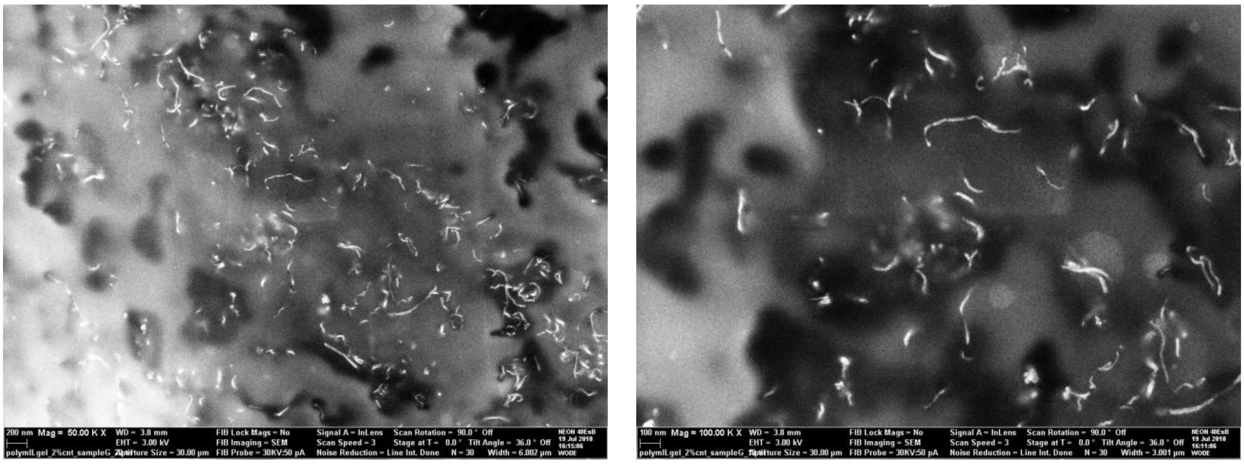

Figure 11. Dispersions of CNTs in IL

3.4.2 Alignment and positioning using Electric and magnetic fields

The aim of this activity was to achieve the alignment and positioning of CNTs in the polymeric matrices in order to improve their electrical properties (alignment) and their tribological behaviour (subsurface positioning).

During the tasks different approaches have been used in order to achieve the above mentioned aim. Thus, electrical DC and AC fields have been used to align the CNTs. Approaches used in previous tasks (ionic liquids and block copolymers) have also been combined with the electrical field strategy.

The overall results obtained in the task are summarized in the following table 2

Table 2. Summary of alignment using electric and magnetic fields

Partner	**ECNP**	**EHU**	**UBA**	**UBA**	**CIDETEC**	**CIDETEC**
Type	DC/magnetic field	AC	AC	AC	DC[1]	DC[2]
Matrix	Epoxy /PA	Epoxy	Epoxy	Epoxy	Epoxy	Epoxy
CNTs	ARKEMA/UBA	ARKEMA	ARKEMA/UBA	ARKEMA	ARKEMA	
Direction	Both width and Thickness	Width	Width	Thickness		Width
Amount of CNTs (%wt)	0.1, 0.5, 1	0.01; 0.05; 0.1[b]	0.05; 0.1; 0.2 / 0.5	0.04-0.2	0.1	0.024-.1
Conductivity	Surface conductivity 10^{-5} – 10^{2} S/m	Not measured	$1.1x10^{-3}$ S/m by electric fields / Superficial conductivity 5.12 $x10^{-5}$ S/m by	1.4 $x10^{-5}$ S/m	10^{-6} -10^{-8} *S/m*	10^{-7}-10^{-6} S/m

			magnetic fields			
Alignment	Yes	Yes	Yes by electric fields / No by magnetic fields	Yes	No completely	Doubtful

The results obtained allow t concluding that t**he alignment of the CNTs in the polymeric matrices has been achieved by different methods. This alignment allows to improve the conductivity of the samples in different amounts depending on the method used:**

The type of CNTs used has an influence on the alignment under electrical fields. Commercial CNTs from ARKEMA and laboratory CNTs from UBA have been used. The best results have been obtained with commercial CNTs from ARKEMA.

The alignment of the CNTs is possible under DC fields. The influence of functionalization with -COOH groups was also examined. According to values obtained the COOH-functionalized carbon nanotubes using DC fields leads to the highest values in terms of conductivity. For both 0.1% wt and 1% wt of CNTs conductivity values in the range of 10^2 S/m have been obtained. This is a significant improvement as neat matrices has values around 10^{-11}.

The use of AC fields also promote the alignment of CNTs. Values of conductivity around 10^{-6} S/m can be achieved by adding a low quantity of CNTs (0.05% wt). In this case lateral clustering of CNTs have been observed due to the electrophoretic effect. The analysis and control of the process variables have led to avoid lateral clustering in the nanocomposites allowing to obtain films with good conductivities (1.11 x10^{-3} S/m) for a CNT content of 0.2 wt. %.

The use of ionic liquids combined with electric fields leads to an improvement in the dispersive behavior of CNTs. Nevertheless the degree of alignment obtained is doubtful. A little improvement in terms of conductivity has been observed (10^{-6}-10^{-8}).

The lamellar structures of block copolymers can be promoted applying electric fields. This is an interesting result in connection with the nanostructuring of block copolymers strategy (figure 12).

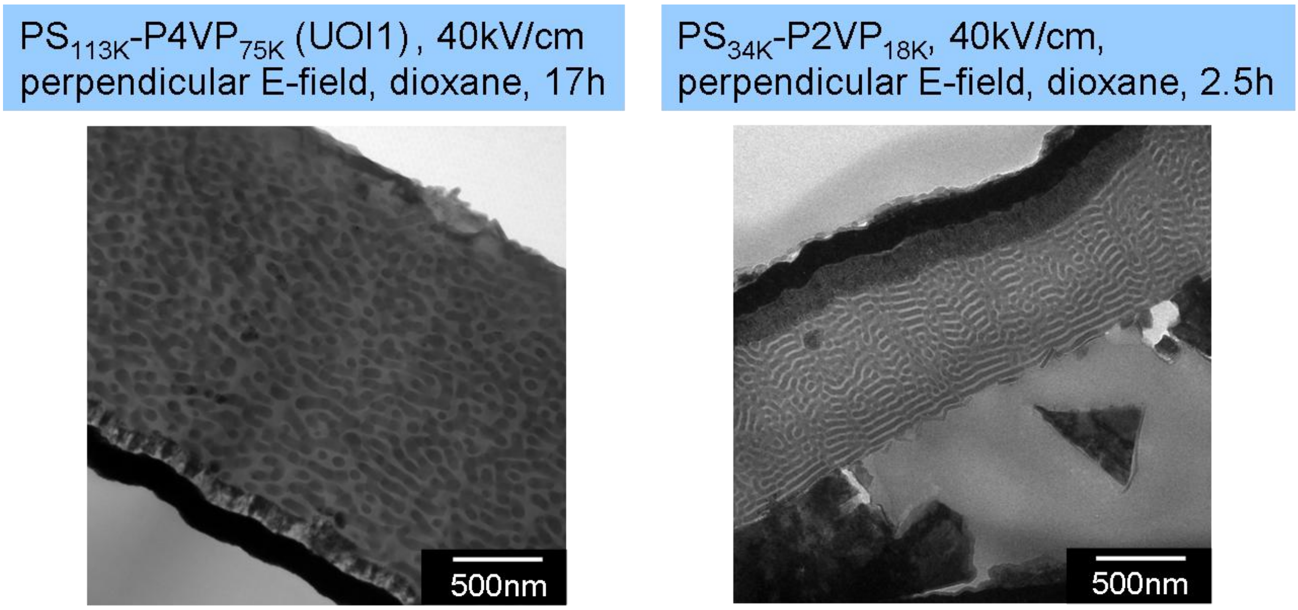

Figure 12. Cross-sections of oriented lamella by electric field in BC films

An improvement of the conductivity was obtained when applying small magnetic fields (1.17 mT). On the other hand, higher magnetic fields (1 T) can lead to the surface positioning of the magnetic CNTs devoleped by UBA. This result leads to values of conductivity about 10^{-5} S/m. Additionally, the subsurface positioning of the CNTs also leads to an improvement on wear and hardness.

The alignment of CNTs on PA matrices was not achieved due to the difficulties imposed by the processing of PA matrices.

Together with the experimental approaches, ECNP has developed a model of orientation of CNTs in viscous media under the application of electric fields to correlate the degree of orientation with time. The model was validated by an experimental set up founding good agreement between experiments and model predictions. This model is very useful to control the processing conditions as it relates the degree of orientation and processing time which is important to find a balance between orientation and curing time of the epoxy matrices.

3.5 Processing and properties of nanocomposites

Different processing techniques were studied during the project to manufacture the CNT/polymer composites depending on the polymeric matrix, final application and current industrial equipment. In this sense, the influence of the use of CNTs and the adaptation of the processing routes to include carbon nanotubes have been analyzed. The final properties of the final nanocomposites were analyzed.

The main technologies used and applications were the following

- Pultrusion processes for glass fiber and carbon fiber thermosetting composites for construction applications.

- Vacuum assisted processes to obtain carbon fiber/epoxy for aeronautics structural applications.
- Solvent processing and spraying for aeronautics coatings applications.
- Extrusion and injection processing for Glass fiber/PA composites for automotive applications.
- Solvent processing and extrusion processing for PLLA for biomedical applications.

The results obtained are shown in the following sections.

3.5.1 CNTs dispersion

One of the main problems associated with CNTs is that they tend to agglomerate due to van der Waals interactions between tubes. This represent problem as CNTs need to be well dispersed inside the matrices in order to improve their properties. Moreover, the presence of CNTs agglomerates inside the matrix can weaken the properties of the final nanocomposites as they may lead to failure, due to poor wetting of CNTs by the matrices and because clusters of CNTs inside the matrix may act as crack initiators.

For this reason, different dispersion methods were analyzed in the project. On one hand, the functionalization strategy already mentioned in previous sections demonstrated to be useful to improve the dispersion of CNTs in different solvents. For instance, the use of modified PLLA with different chemical groups as pyrene or imidazolium as dispersing agents (and the use of other molecules as DO3) showed a significant improvement on the dispersion of the CNTs in PLLA matrices. The combination studied by UMONS of PEO-b-PLLA with LiCl salts have shown a significant improvement in the dispersion leading to percolation thresholds for quantities of CNTs as small as 10^{-3} wt%

On the other hand, the use of block copolymers is helpful to improve the dispersion of the CNTs, as shown in the previous sections.

Besides the above mentioned strategies different mechanical dispersion methods such as rotational mixing, ultrasounds, and three roll mill were analyzed by ECNP, ACCIONA and EADS during the project. The three roll mill showed the best results in terms of dispersion (figure 13) and proved to be a suitable up-scalable method that can be used for stable dispersion in epoxy matrices. Nevertheless some advances were done by ECNP in the rotational dispersion tools. The new rotational dispersion tools developed have a potential future exploitation and will be promoted for protection by the application for a utility model.

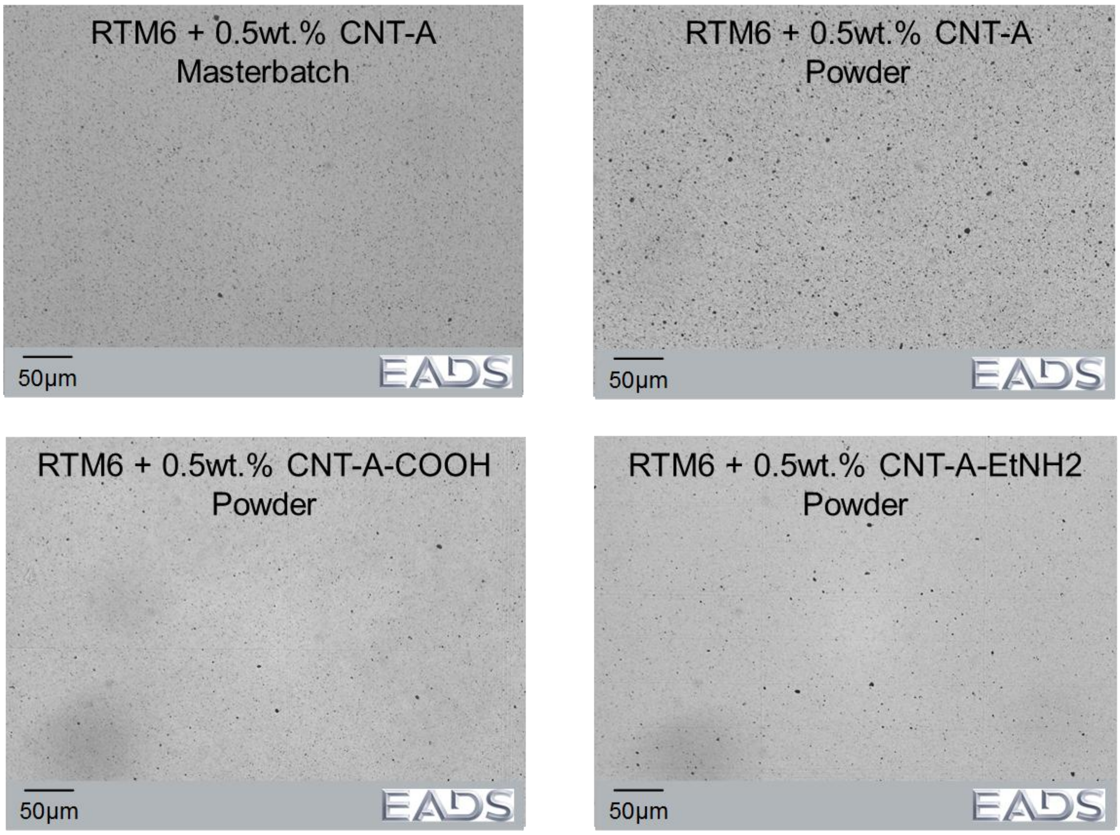

Figure 13. Microscopy pictures of CNTs dispersions produced by three roll mill using an epoxy based masterbatch (top left), commercial CNTs in powder form (top right) and CNTs functionalized with COOH (bottom left) and amine (bottom right) groups.

3.5.2 Viscosity of nano-modied resins

Another problem that the use of carbon nanotubes introduces at the processing stage is the increased viscosity of the resins due to the CNTs. This increase of the viscosity is a big drawback as the resin cannot be processed as usual.

ACCIONA has studied the influence of the CNTs on the viscosity and how the amount of CNTs used can affect the workability and the storage of the resins containing CNTs.

They found 0,2%wt of CNTs content presented the best balance at room temperature between workability and storage of the resins.

The same behaviour was observed by EADS. Although the use of functionalized CNTs can limit the increase in viscosity compared to unfunctionalized CNTs, this increase occurs for low quantities of CNTs (figure 14).

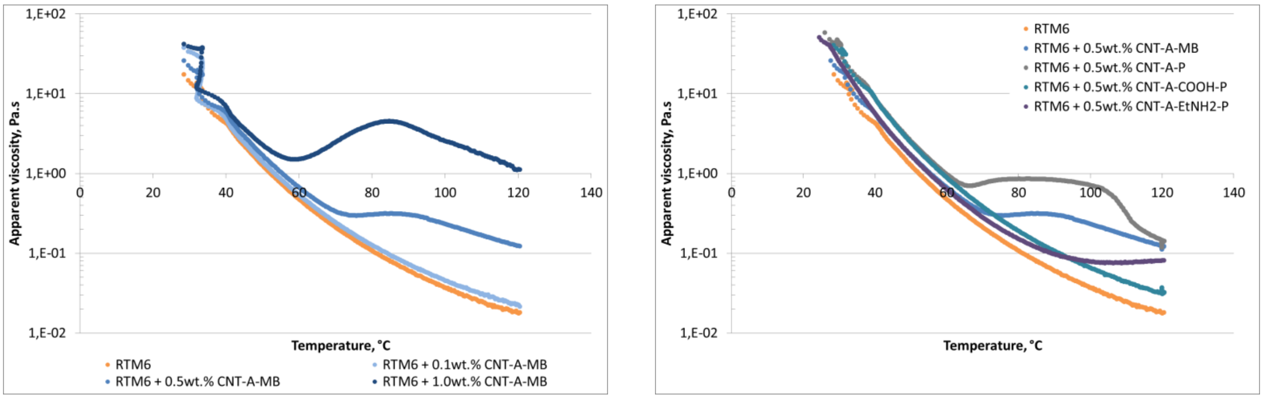

Figure 14. Viscosity of nano-modified resin

3.5.3 Pultrusion processing for construction

In despite of the viscosity problems mentioned above ACCIONA has been able to obtain glass fiber and carbon fiber thermosetting based composites by means of pultrusion processing. In both cases the optimization of the the pultrusion parameters was required to adapt the process to the nanomodiied resins. In the case of glass fiber based composites a low quantity of CNTs (0.2% wt) was used to overcome the above mentioned viscosity process. Pultruded profiles were successfully processed but the low quantity of CNTs used does not allow to improve the mechanical properties. In the case of the carbon fibers pultruded profiles, predispersed masterbatches supplied by ARKEMA were used. The use of masterbatches together with control of the processing parameters allowed to use 2% wt of CNTs. **The mechanical properties of the pultruded profiles were tested and improvements between 5% and 10%** (depending on the property see figure 15) was achieved.

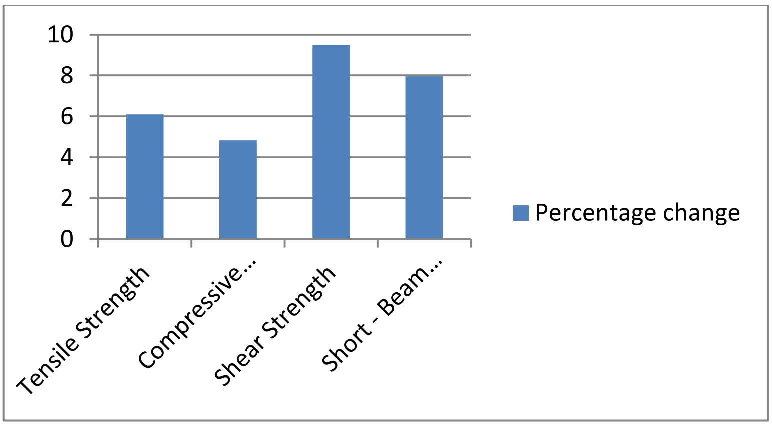

Figure 15. Percentage variation of mechanical properties due to the inclusion of CNTs in the matrix in pultruded carbon fiber epoxy composites.

3.5.4 Vacuum assisted processing for aeronautics

The nanomodified resins were manufactured by means of a vacuum assisted process to infuse the resin inside fiber preforms made of non-crimp fabrics (NCF carbon textiles) in order to obtain carbon fiber composites reinforced with CNTs. The processing of such as composites was a real challenge.

Together with the viscosity problems, the attempts of infusing the nanofilled resin inside the NFCs were initially unsuccessful as the CNTs in the resin are filtered by the NFCs avoiding an appropriate infiltration of the nanofilled resin and leading to the reagglomeration of the CNTs. ECNP has proposed a new modified vacuum assisted process which helps to infuse the nanofilled resins in a more homogeneous way. This result will apply for protection under a utility model application.

The second envisaged method to obtain nanocomposites for aeronautics application is to use high temperature thermoplastic (HTTP) films, which would contain the CNTs. These films could then been inserted between the carbon plies (figure 16).

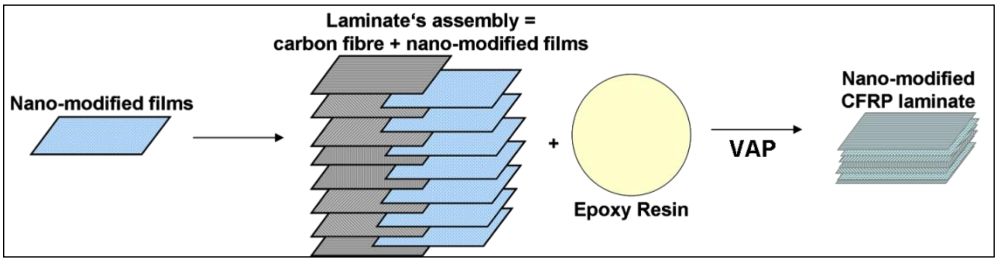

Figure 16. Envisaged method to incorporate the CNTs in CFRP

Different HTTPs modified with CNTs were analyzed in terms of compatibility with the epoxy resin matrix. Although, the mechanical properties of the final laminate improved due to the use of HTTPs the addition of CNTs does not bring any further improvement.

To overcome the above mentioned problems, EADS has developed a methodology to process the carbon fiber reinforced composites including CNTs by means of a combination of spraying and infusion techniques. The details of the processing will be used by internally by EADS and are subject of industrial secret. The processed materials showed improvements in mechanical properties such as interlaminar shear strength of about 15%.

3.5.5 Coatings for aeronautics application

During the project, coatings containing CNTs for aeronautics applications were developed. The objectives were to obtain nanocomposite coatings with improved electrical properties (for antistatic applications) and improved resistance to wear, abrasion and hydrophobicity. The use of aligned and positioned CNTs is a way to improve the electrical properties using low quantities of CNTs, as mentioned in previous sections. Surface properties were analyzed also for randomly distributed CNTs both from Arkema and the magnetic CNTs from UBA, as well as coatings containing block copolymers. The inclusion of hybrid MWCNTs+Hercynite ("magnetic CNTs") increases slightly the hydrophilicity of the samples when compared with the neat resin. On the other hand an improvement these nanocomposites show a decreased wear rate and a reduction of the friction coefficient as well as an increased hardness that indicate a strengthening of the epoxy matrix when using hybrid nanofillers.

Contact angle values increased significantly with the addition of ep52SBS with respect to each unmodified epoxy system due to the hydrophobic nature of the block copolymer. On the other hand, the presence of COOH functionalized MWCNT showed the opposite effect on surface hydrophobicity. For a particular block copolymer content, a decrease in contact angle measurement with the increase of a-MWCNT content was observed. This decrease was probably due to the acid treatment on nanotubes. Wear tests showed that the addition of block-copolymer (> 5 wt%) is detrimental for wear resistance and on erosion resistance and should not be used. The coefficient of friction of BC modified coatings is in the range of the unmodified epoxy layer. There is a limited increase on erosion resistance by CNT modification.

The results of the contact angle measurements show that the main parameter that affect this parameter is the CNTs dispersion level; in particular higher is the dispersion level higher is the water contact angle. The addition of CNTs on bulk epoxy nanocomposite leads to an improvement of the wear rate. Nevertheless the alignment of the CNTs using an electric field does not show any improvement when compared to randomly dispersed CNTs. No positive effect on erosion properties could be detected for CFRP composite bulk material with CNT concentrations of 0.5 wt%.

Although solvent based techniques were analyzed for the processing of coatings containing CNTs, the final focus was made on spraying techniques has they are more suitable for industrial applications and therefore was selected for the demonstrator.

3.5.6 Glass fiber polyamide containing CNTs for automotive applications

The objective from the automotive point of view was to develop a new compound based on structural polyamide glass reinforced and filled with carbon nanotubes in order to confer electrical properties for automotive applications, in particular to enable the E-coating process on a plastic based component.

Polyamide reinforced with glass fibers containing CNTs were processed by means of extrusion and injection techniques. The parameters of the different steps of the process were analyzed at a laboratory scale by ECNP and up-scaled and optimized for industrial scale processing by INTECO and CRF. The use of nanotubes in powder form and in predispersed masterbatches (both provided by ARKEMA) were analyzed. The used of predispersed masterbatches was selected as the most suitable for industrial implementation. Thus, the dispersion mechanism of the CNT in the neat PA matrix was investigated to allow further improvement in the masterbatch preparation. In this sense formulations of the masterbatches adapted to the PA grades used are required.

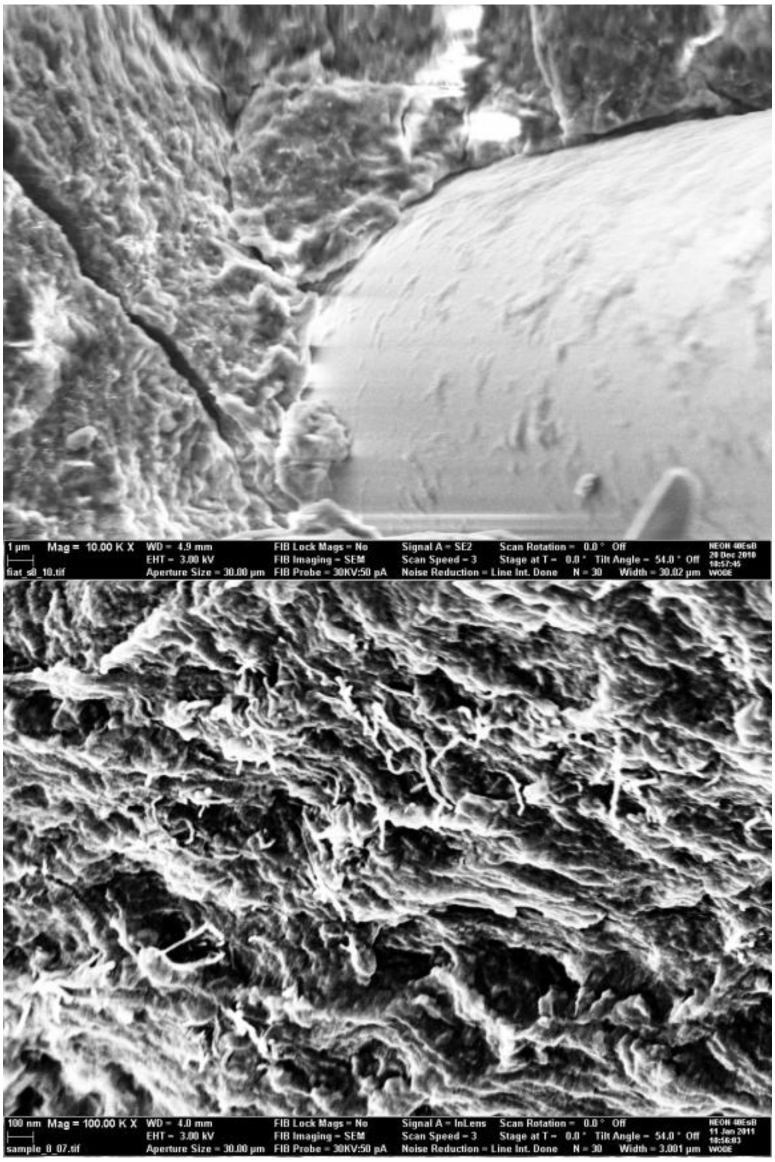

Figure 17. Fracture surface of PA-GF-CNTs nanocomposites showing good wetting of the polymer on the fibres (top) and well dispersed CNTs (bottom).

Initially, the focus was to identify a sufficient amount of CNT to guarantee the required electrical conductivity and the influence of amount of glass fibres. Then, the different formulations and processing parameters were analyzed in order to obtain nanocomposites with improved electrical properties maintaining the mechanical properties of the glass fiber based composites.

INTECO succeed in the manufacturing of such composites at an industrial level. An amount of 300 kg of such material has been produced for the demonstrator. The material was injected by CRF and it was successfully coated using E-coating process.

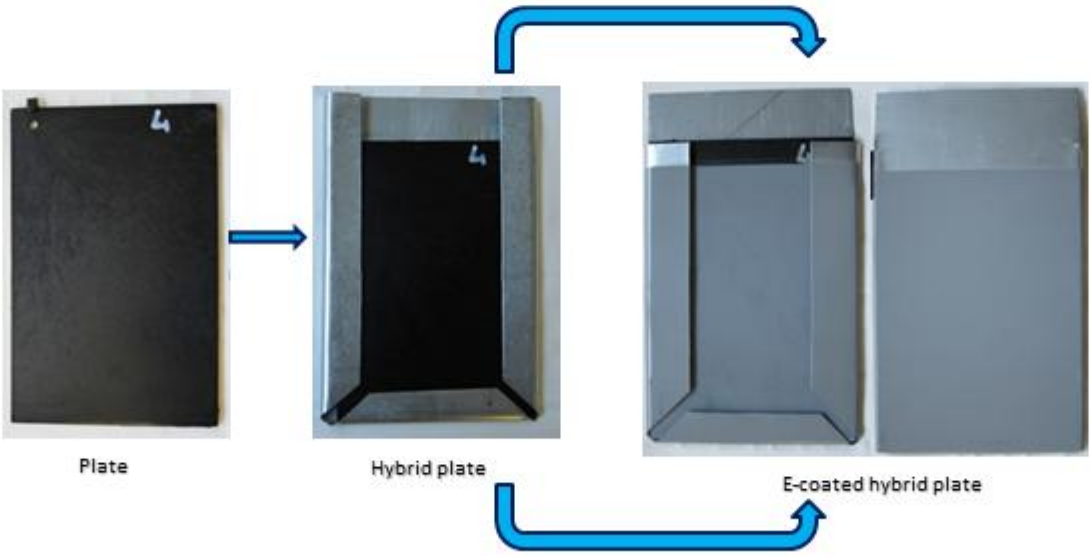

Figure 18. E-coated hybrid metallic-nanocomposite plates.

The results obtained have a great potential for a short term industrial implementation. For this reason the details of the formulations and processing parameters will be kept as industrial secret by CRF for their further use.

3.5.7 PLLA-CNT based composites for biomedical applications

Poly(lactide)s (PLA's) are used for medical and pharmaceutical applications. Examples are screws and plates for fracture fixation. There is a strong wish from the market for stronger degradable materials in order to be able to replace metallic implants by polymeric, degradable implants. The incorporation of CNT in PLA may be a useful way to increase the mechanical properties of the material to such a level that polymers may be used in more applications than currently possible.

To this regard the main requirements are initially two: the new material must be safe (from the toxicity and health point of view) and a significant improvement of the mechanical properties. If this requirements are fulfilled the new materials will demonstrate its interest to be used on implants usually made by metals, such as screws and plates for fracture fixation.

EMPA has analyzed in vitro the effects of multiwalled CNT (MWCNT) in simulated bone niche. To understand the mechanisms by which dispersed MWCNT are perceived by living cells, three types of human primary cells were grown in the presence of different concentration of MWCNT. Special emphasis was made in defining reliable tests to assess the biocompatibility of the CNTs. The PLLA/CNT nanocomposites were studied in depth as they will be used directly in contact with the body.

EMPA evaluated MWCNT of Arkema but also MWCNT from another source, Nanocyl. Preparation of efficient and homogenous suspension of MWCNTs is crucial for reproducible and reliable in vitro tests. Pluronic F-127 was used as dispersing agent as improved the dispersion of CNT and is non-toxic for cell activity, according to the ISO 10993-5.

The results showed that carbon nanotubes are taken up by human bone marrow derived mesenchymal stem cells (HBMC) when cultured in the presence of the MWCNT. No evidence that cell functionality was affected by the uptake of MWCNT. HBMC proliferation as defined by cell density, metabolism as defined by the conversion of MTS to its formazan form and rate of cell death as measured by FACS were not affected by this uptake treating the cells with 3.75-30 μg MWCNT/ml for 1-5 days.

The bioacceptance (absence of cytotoxic effects, cell adhesion and spreading, bioactivity (cell proliferation and differentiation) of PLLA/MWCNT composite containing different concentration of MWCNTs (0.1, 0.5, 1 wt.%) has been carefully studied. The results show that no toxic compounds are released from the composite in cell culture medium when standard extract test (ISO 10993-12) using 3T3 fibroblastic cells was performed and that HBMC attach and spread on the composite surface. Moreover our data show that HBMC cells keep their potential to differentiate toward (pre-) osteoblastic stage, as verified by expression of osteogenic markers.

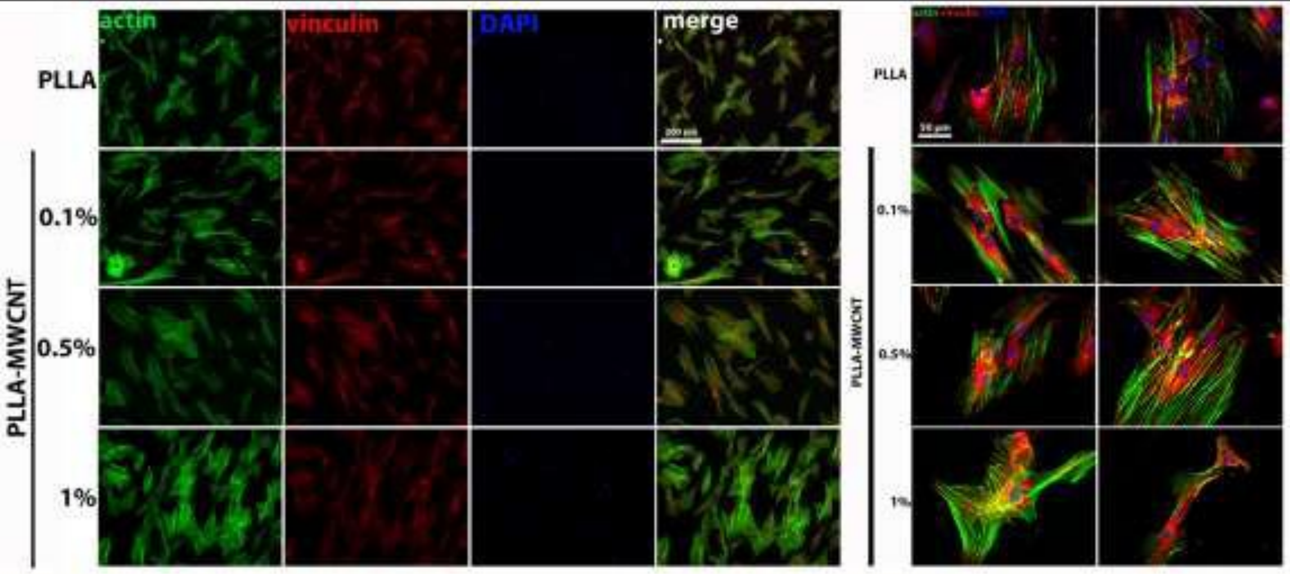

Figure 19. Immunofluorescence analysis of F-actin and vinculin distribution in HBMC cultured on PLLA/MWCNT composite. Scale bar: 200 μm and 50.

In this sense, the results from biotoxicity test are encouraging as no harmful effect was found in the set of tests performed.

Regarding the mechanical properties, PLLA matrices filled with different amount of as received CNTs does not show any improvement in the mechanical properties. This is attributed to a bad dispersion of CNTS for this reason further strategies involved the use of different dispersing agents.

PLLA-b-PDMAEMA functionalized CNT PLA nanocomposites (by UMONS) were tested by EHU. The results showed some slight increases of rigidity (Young's modulus) up to 23% for 3% wt of CNTs with respect to the nanocomposites with uncoated nanofiller. Unfortunately, the tensile and impact strength properties decrease, whereas a lower nominal strain at break is also noticeable.

In nanocomposites processing using hot-press and containing quantities as low as 0.1 % of MWCNTs, Young's modulus increases, in around 45 %, from the PLLA/py-end-PLLA24900 blend to the nanocomposite containing CNTs. This noteworthy effect is associated to the strong interfacial adhesion and proper dispersion of the fillers in the polymer matrix. Consequently, the addition of pyrene-end-PLLA achieves higher strength of the matrix. The increase of Young's modulus is followed by the decrease of the elongation at break. This is because as the filler content is higher, the brittleness of PLLA increases.

The use of DO3 dye as dispersing agent was investigated by UBA. Although, this kind of material could not be used for biomedical applications because of the toxicity of the DO3 dye, the combination of MWCNT-DO3-PLA is a promising idea for the implementation of these new materials as electrical-optical-sensors. An adequate dispersion of MWCNT in a PLA matrix using DO3 as a surfactant was obtained, to achieve electric conductive, optically active composites with better wear resistance than PLA matrix. With only 0.3 wt % MWCNT, the electrical conductivity of the material was 1.6 x10-1 S•m-1. In addition, the material kept the optical properties of the dye in terms of absorbance bands. The simultaneous use of DO3 and MWCNT as nanofiller in PLA composites, allows the development of new materials with better mechanical properties of neat PLA. By varying the MWCNT content, different tailor made materials could be achieved. If the MWCNTs are well dispersed (low concentrations), nanocomposites having high toughness, high strain at break and high strength at break can be obtained. While for higher concentrations than 0.3 wt %, the nanocomposite presents better mechanical properties than PLA, in addition to electrical conductivity and optical response.

So, although the results on biotoxicity were positive, the level of improvement on the mechanical properties is not considered enough to consider this material for biomedical applications. For this reason, further development of these results must be done in order to improve the mechanical properties. In conclusion, the commercial exploitation of the PLLA-MWCNTs based materials for biomedical use is not applicable at this time.

4. The potential impact

According to BCC research study on the market forecast for CNTs, the global market for various carbon nanotubes reached $192 million in 2011. This market is expected to grow reaching $239 million in 2012. The forecast for the next five years estimates an annual growth rate of 22.4% to go beyond $500 million by 2016. The expected growths for the different nanotube grades are not the same. Thus, the market for multi-walled carbon nanotubes (MWNTs) is estimated to increase a 9.1% between 2011 and 2016 while in the case of few walled CNTs (FWCNTs) the expected growth is 131.6% between 2011 and 2016.

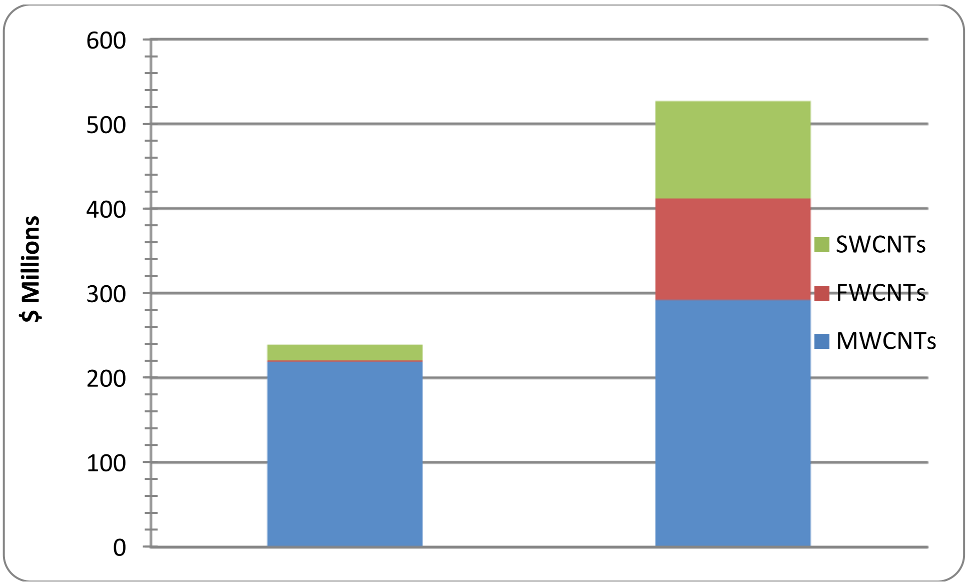

Figure 20. Global market for CNT grades based on data from BCC Research

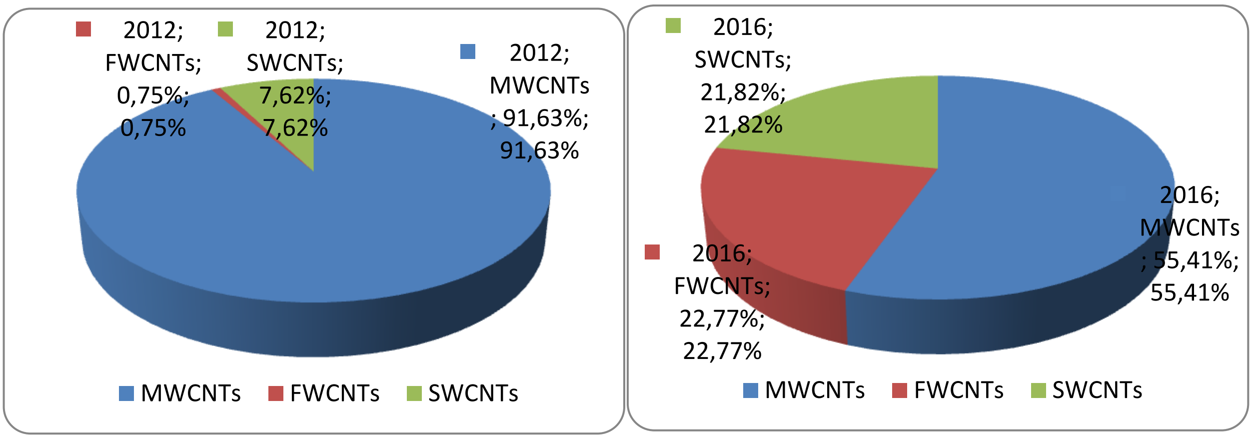

Figure 21. Market shares for different nanotube grades based on data from BCC research. Left. 2012. Right: 2016

Thus, the market for few-walled CNTs is the one expecting a more important increase. In this context, the results of the project in the field of the controlled growth of CNTs are especially significant. **The studies of carbon nanotube growth performed within the POCO project have a real potential for industrial use. In this sense ARKEMA, CNRS, UBA and EHU have applied for 4 different patents to protect the results developed in the project.**

A report on Global CNT market of Nanotech Insights (July 2011), estimates that the main market for CNTs in 2010 was for plastics and composites with a market share of 69% for a $472.9 million in sales with the expectation to remain the most significant market for CNTs in 2016. The same report foresees an average price reduction of 15% in the next five years. This price reduction will enable the possibility of commercial exploitation of the results obtained in the project.

The project has developed different strategies to be specifically (but not only) applied in four different sectors: aeronautics, automotive, construction and biomedical.

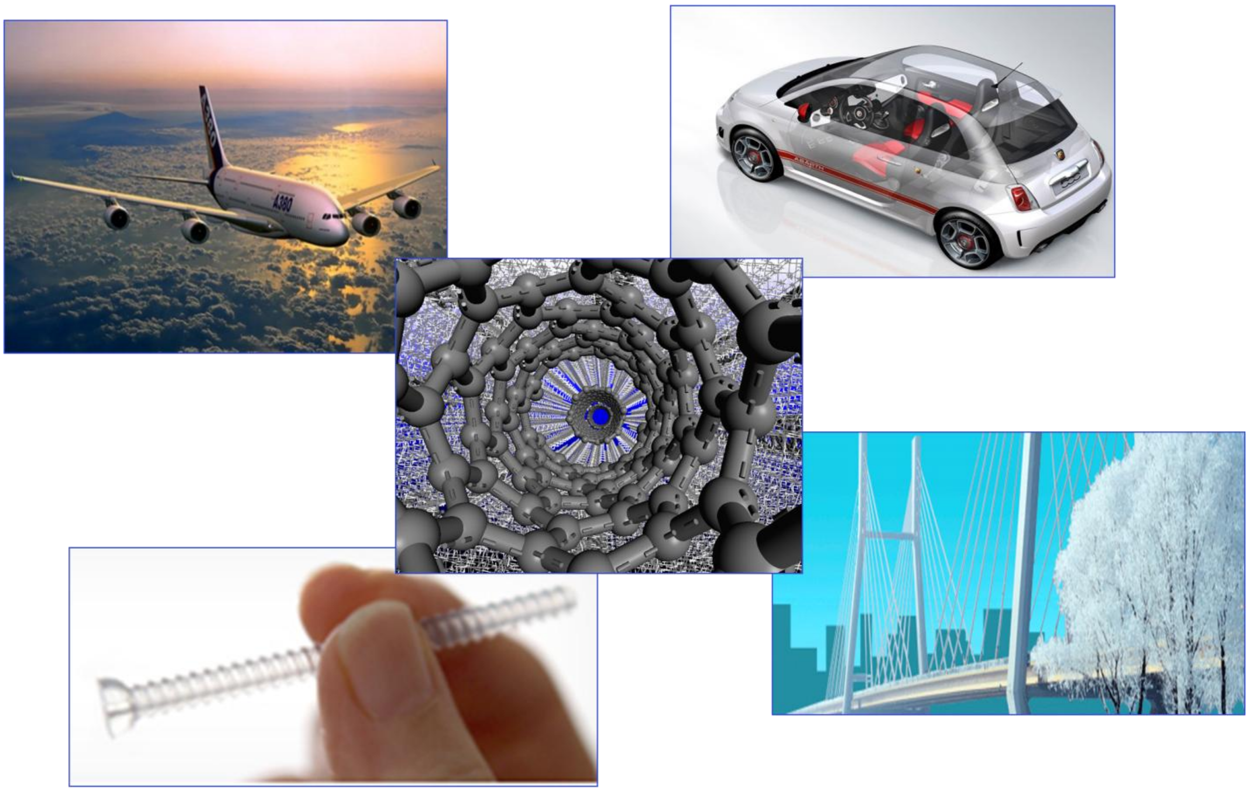

Figure 22. Target applications in the POCO project.

In 2010, the number of automotive vehicles (including cars, trucks and buses) in operation worldwide exceeded 1 billion for the first time. On the other hand fuel consumption is still one of the major operational costs in aviation. Therefore, in current scenario of increased fuel costs and strict regulations on CO2 emissions, one of the main interests of transport industries (in this case automotive and aeronautics) is to obtain lightweight materials to reduce fuel consumption and CO2 emissions. In this context the use of polymer based composites will play a crucial role in the next future to reduce the weight of vehicles. In addition for auto manufacturers, a switch to advanced nanostructured composite solutions would mean fewer parts, cheaper and less complex manufacturing equipment. On the other hand the use of CNTs can bring interesting functionalities to polymer based composites as increased mechanical properties and electrical properties. Different automotive parts can take advantage of the technological developments in POCO project: hood, tail gate, door, floor, upper and underbody. Considering Fiat target on weight reduction for 2020, it can be estimated the use of the POCO concept material in bonnets, tailgates, floor parts, for an amount of around 15 kg of material for each car. This amount can be equal to 8 kg of weight reduction in a car body. Initially the material could be introduced in the higher segments of cars and could be estimated 300.000 vehicle/years that means 4500 tons of nanocomposite (around 100 tons/year of carbon nanotubes).

Construction industry is experiencing a significant increase in the use of composite structures. The use of composite materials in construction is a market with a great potential in the following years, in which growths of more than 400% with respect to the current market are expected. These composites are typically combinations of high-strength fibres and resin matrices, to offer significant benefits in strength, weight and service life performance over traditional materials. But, it is necessary to reduce the fibre quantity used to obtain a specific mechanical reinforcement with a subsequent decrease of the cost and weight of the final material, obtaining a competitive product which will make easier the transport and will increase the shape possibilities and prefabricated pieces. The replacement of long fibres by carbon nanotubes will substantially reduce the density of the final composites, being necessary to achieve the suitable transfer of the intrinsic properties of carbon nanotubes (CNTs) into high-performance composite materials.

It is important to remark that CNTs will not necessarily substitute current fillers used in composites for structural applications, such as carbon fibers and glass fibers. On the contrary, it is expected that CNTs will be used to reduce the carbon/glass fiber content, to improve the mechanical of such composites and/or to bring new functionalities through improved properties such as electrical properties.

During the project, different strategies were employed in order to bring these improved properties and new functionalities to polymer based composites.

Thus, the mechanical properties of carbon based composites were improved for construction and aeronautics structural applications by using CNTs. The percentage of improvement achieved varies between 5% and 15% depending on the property. Moreover, **the project succeeded to overcome some important problems related to the processing of CNT based nanocomposites, generating an important knowledge on processing conditions of industrial interest for the companies involved in the project.** As a specific technological results **new processing devices to improve the dispersion of CNTs and to improve the processability of nanofilled CFRP** (by using a new vacuum assisted process) were developed in the project and will be protected by utility models. An improvement in the transverse electrical conductivity and self-sensing properties of the composite is also expected with further work.

The results obtained and the advances on the processing of the CNT based nanocomposites are encouraging and will be the basis for further development by ACCIONA and EADS to achieve the targeted final properties and subsequent commercialisation. In this sense, the work in the frame of

POCO has demonstrated the technology readiness of CNT-modified carbon fibers reinforced polymer parts.

The know how developed in POCO will be used by EADS in other projects such as, Electrical and Saristu where the incorporation of Carbon Nanotubes into aeronautical resins is expected to enable weight savings of up to 3% when compared to the unmodified skin/stringer/frame system, while a combination of technologies is expected to decrease Electrical Structure Network installation costs by up to 15%.

Regarding the electrical properties different strategies were developed in order to improve the conductivity of the nanocomposites. Thus, **the electrical properties of polymer based coatings for aeronautics applications have been also improved by the use of CNTs to reach levels that allow their use for antistatic protection.** On the other hand, **automotive parts made on glass fiber polyamide based composites filled with CNTs were manufactured using industrial scale equipment during the project**. **The electrical properties of these nanocomposites**, allow the use E-coating techniques and therefore **enable the use of this material to manufacture hybrid metal/nanocomposite parts of reduced weight to substitute in the short term structural metallic parts in the automotive industry.**

Figure 23. Automotive bonnet containing CNTs manufactured in the project.

Concerning the biomedical application the project analyzed the potential of CNTs to be used as reinforcement in PLLA biodegradable polymers for bone repair medical implants. It is well known that one of the main concerns of scientific community and society regarding the use of CNTs (and nanoparticles in general) is their potential toxicity and how they can affect the human health. This is especially important in the case of biomedical devices working directly in the human body. Thus, in order to have suitable materials for this use the nanocomposites must be safe from the biocompatibility and cytotoxicity point of view as well as able to increase significantly the mechanical properties of the neat polymer. Important efforts were dedicated to the reliability of the toxicological tests arranged in the project. According to tests performed in the project, **no evidence that cell functionality is affected by the MWCNT** on tests on human bone marrow derived mesenchymal stem cells (HBMC) was found. **Moreover, the results on bioacceptance tests show that no toxic compounds are released from the composite in cell culture medium.** Although, some improvements in the mechanical properties of PLLA were obtained when using CNTs properly dispersed, **further research will be necessary in order to increase the final properties of these composites to become a reality for the biomedical industry.** Nevertheless, some of the results obtained have shown interesting properties that could be useful in the packaging industry.

In summary, different several technological developments interesting for industrial use and exploitation (in short, medium and long term) were obtained in the project. Some of them will be protected by patents (4 patent applications) and other by utility models (2 applications under preparation), while some other will be kept as industrial secret by the industrial partners to use them internally for further development until more degree of maturity is reached.

Besides the industrial developments, important results from the scientific point of view have also been achieved. Thus, different strategies of functionalization, alignment and positioning of CNTs, the use of ionic liquids and the nanostructuring and confinement of CNTs in block copolymers have been studied, contributing to increase the scientific knowledge on the field of CNTs/polymer composites. Some of them such as the different new functionalizations developed or the alignment and positioning of CNTs by means of electric and magnetic fields have succeed to show their potential to improve the final properties of the nanocomposites at laboratory level. In this sense, the promising results obtained would require further up-scaling of the devices and processes to be applied at industrial level. It was demonstrated that the conductivity values can be improved with low CNT contents when they are aligned by the application of electrical fields during the processing; the positioning of the CNTs on the subsurface the polymers by the application of magnetic fields have shown interesting improvements in wear behaviour and hardness of the composites; the different functionalizations have led to better dispersion and processability of the nanofilled composites. The role of the CNTs on the crystallization of semicrystalline matrices was also studied showing that CNTs can act as nucleating agents and conditions (in terms of functionalization and role of block copolymers) to confine the CNTs in selected phases of nanostructured polymers were defined.

As a result of these scientific achievements more than 24 articles have been published in relevant peer-reviewed scientific journals. Besides the publications in scientific journals, more than 65 dissemination actions and also disseminated in different scientific forums such as conferences and workshops related to the nanocomposites field as well as in general public targeted publications. It is worth to mention that both academic and industrial partners have been involved in the dissemination activities in the project. Moreover, **13 Ph.D. theses were developed with results (totally or partially) obtained of the project. 4 of them have been already successfully defended while the others are expected to be defended in the short term.**

The partnership of the project has been successful to establish a good network of collaboration between academic and industrial partners. Thus, academic partners have worked taking into account the requirements established by industrial partners. On the other hand, different training actions, with the participation of experts from inside and outside the consortium, have been developed targeting the students and the industrial partners. In addition, different mobility actions were promoted inside the consortium involving both partners from industry and academia. Besides the more mature technological developments many of the strategies developed in the project leaded to interesting proofs of concept that may require further research to be used industrially in the next future. In this sense further collaboration between different partners is expected to continue beyond the project.

5. Contact details

Coordinator: Borja Coto (bcoto@tekniker.es)

Address: Fundación Tekniker. c/ Iñaki Goenaga, 5. 20600 Eibar · Gipuzkoa. SPAIN.

Project website: www.poco-projec.org. (poco@tekniker.es)

Partner	Contact
TEKNIKER	Borja Coto. bcoto@tekniker.es. c/ Iñaki Goenaga, 5. 20600 Eibar · Gipuzkoa. SPAIN. www.tekniker.es
ARKEMA	Patrice Galliard. patrice.gaillard@arkema.com
EADS	Matthias Geitsbeck. Matthias.Geistbeck@eads.net
IPF Dresden	Manfred Stamm. stamm@ipfdd.de
University of Mons	Philippe Dubois. Philippe.dubois@umons.ac.be Jean-Marie Raquez. Jean-Marie.Raquez@umons.ac.be
Universidad del País Vasco	Jose Ramón Sarasua (EHU Bilbao). jr.sarasua@ehu.es Galder Kortaberría (EHU San Sebastian). galder.cortaberria@ehu.es
SOLVIONIC	Sebastien Fantini. sfantini@solvionic.com
ECNP	José Kenny. kenny@ictp.csic.es; kenny@unipg.it
PURAC	Tom Uitslag. t.j.uitslag@purac.com Marc-Anton Kruft. m.kruft@purac.com
CIDETEC	Pedro Mª Carrasco. pmcarrasco@cidetec.es

CNRS	Philippe Serp. philippe.serp@ensiacet.fr
IN.TE.CO.	Gabriele Nicola. g.nicola@maipsrl.com
ACCIONA	Isaac Sánchez. CenAg152@acciona.com
CRF	Andrea Pipino. andrea.pipino@crf.it
University of Ioannina	Apostolos Avgeropoulos. aavger@cc.uoi.gr
University of Buenos Aires	Silvia Goyanes. sgoyanes@gmail.com
EMPA	Arie Bruinink. Arie.Bruinink@empa.ch