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MODCOMP

"MODIFIED COST EFFECTIVE FIBRE BASED STRUCTURES WITH IMPROVED MULTI-FUNCTIONALITY AND PERFORMANCE"

NEXT GENERATION OF CARBON FIBRE BASED MATERIALS

This project has received funding from the European Union's Horizon 2020 research and innovation programme, European Research Council (ERC) under the European Union's Horizon 2020 research and innovation programme, Industrial Technologies, Advanced Materials and Nanotechnologies, H2020-NMP-2014-2015/H2020-NMP-2015, under grant agreement No 685844.

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Follow up project meeting, 3/4 October 2017 Athens, Greece

The month 18 project meeting took place from 3rd till 4th of October 2017 in Athens, Greece.

Project meeting in Athens, Greece

The main focus was on the tasks and deliverables done in the period from the beginning of the project, until the end of September 2017. The first 18 month progress was closely followed by the Project Officer Dr. Achilleas Stalios.

Dr. Achilleas Stalios, Project Officer

MODCOMP recent papers in scientific journals

MODCOMP project partners have been actively working on the articles in different scientific papers. You can access the articles here:

Elias P. Koumoulos, C.A. Charitidis: **Surface analysis and mechanical behaviour mapping of vertically aligned CNT forest array through nanoindentation**: http://www.sciencedirect.com/science/article/pii/S0169433216323625

Eleni Gkartzou, Elias P. Koumoulos and Costas A. Charitidis: **Production and 3D printing processing of bio-based thermoplastic filament:** https://mfr.edp-open.org/articles/mfreview/abs/2017/01/mfreview160010/mfreview160010.html

Pravin Jagdale, Elias P. Koumoulos, Irene Cannavaro, Aamer Khan, Micaela Castellino, Dimitrios A. Dragatogiannis, Alberto Tagliaferro and Costas A. Charitidis: **Towards green carbon fibre manufacturing from waste cotton: a microstructural and physical property investigation:** https://mfr.edp-open.org/articles/mfreview/abs/2017/01/mfreview170001/mfreview170001.html

Elias P. Koumoulos, C.A. Charitidis: **Lubricity Assessment, Wear and Friction of CNT-Based Structures in Nanoscale**: http://www.mdpi.com/2075-4442/5/2/18

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Qi, S., Li, X., Dong, H.: **Improving the macro-scale tribology of monolayer graphene oxide coating on stainless steel by a silane bonding layer:** http://www.sciencedirect.com/science/article/pii/S0167577X1731131X?via%3Dihub

Dimitris K. Perivoliotis, Malamatenia A. Koklioti, Elias P. Koumoulos, Yiannis S. Raptis, Costas A. Charitidis: **Vertically aligned CNT arrays: structural integrity and surface properties:** http://www.emeraldinsight.com/doi/full/10.1108/IJSI-10-2015-0046

Qi, S., Li, X., Zhang Z., Dong, H.: **Fabrication and characterisation of electro-brush plated nickel-graphene oxide nano-composite coatings**: http://www.sciencedirect.com/science/article/pii/S0040609017306910

Aamer Khan, Patrizia Savi, Simone Quaranta, Massimo Rovere, Mauro Giorcelli, Alberto Tagliaferro, Carlo Rosso, Charles Jia: **Low-Cost Carbon Fillers to Improve Mechanical Properties and Conductivity of Epoxy Composites** http://www.mdpi.com/2073-4360/9/12/642

Participation in Conferences and Events

EuroNanoForum 2017

EuroNanoForum 2017

R-Nano Lab attended the EuroNanoforum 2017, that was held in Malta, Valetta, 21-23 June 2017.

This time, ENF was focused on strengthening the competitiveness of EU manufacturing industries through nano and advances technologies and open innovation. In total, 1000 delegates participated in 15 Sessions and 3 Plenaries, while 100 speakers had been invited and 50 exhibitors were presenting their recent achievements.
R-Nano Lab attended the NanoData, Nanosafety, Characterisation and Pilots Workshop, participating in round table discussions and disseminating the current running projects (FIBRALSPEC and MODCOMP).

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Researcher's Night

2017 ΒΡΑΔΙΑ του ΕΡΕΥΝΗΤΗ

ΠΑΡΑΣΚΕΥΗ 29 ΣΕΠΤΕΜΒΡΙΟΥ 2017

Researcher's night is a Europe-wide public event dedicated to popular science and fun learning. It takes place each year on the last Friday in September. Around 30 countries and over 300 cities are involved.

The National Technical University of Athens opened its doors for the fourth consecutive year, organizing the Researchers' Night at the Averof building. NTUA researchers presented their research achievements of MODCOMP project to the general public, aiming at improving the social recognition of researchers, raising awareness and informing the public about research results, and increasing the interest and professional orientation of young people to research professions.

Flyers, leaflets and newsletters were distributed among the participants. Educational videos and samples of carbon fibres and their composites were shown to the public.

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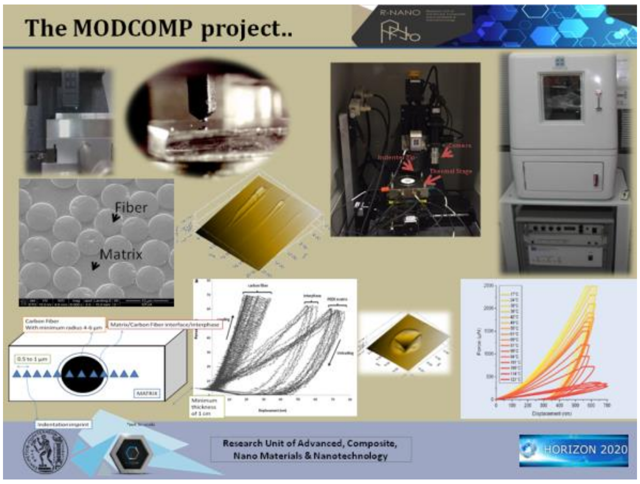
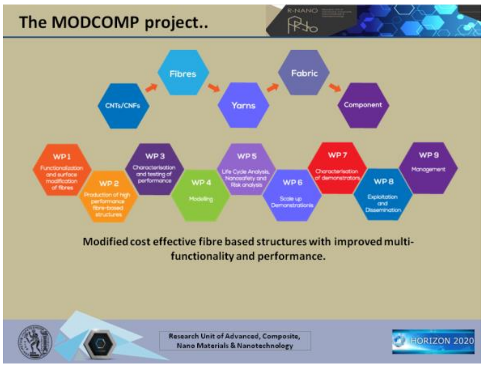
Nano Carbon Enhanced Materials Consortium NCEM-5

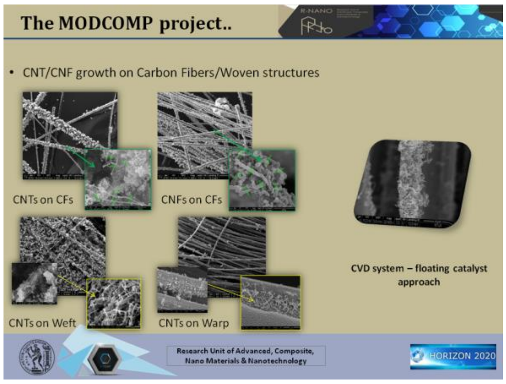
The Nano-Carbon Enhanced Materials (NCEM) consortium provides an opportunity to engage with leading companies in the supply chain and leading world class experts in a commercialisation pathfinder programme for a small fraction of time and total costs of alternatives such as consultancy, meetings, workshops and conferences. The use of nano-carbon materials, such as carbon nanotubes and graphene is a rapidly evolving field and this is an opportunity to influence where it goes and how fast.





The mission of the consortium is to facilitate the commercial uptake of technologies based on nano-carbon materials such as graphene and carbon nanotubes and it brings together potential users from defense, energy, electronics, structural materials, and metal industries with a shared interest in understanding the challenges and opportunities of nano-carbon disruptive technologies.

The aim of the consortium is to provide discussion platform and a vehicle for action regarding collaborative R&D, supply chain building, H&S, regulatory and other issues related to commercialisation of carbon nanomaterials. R-Nano Lab (NTUA) attended the 3rd Meeting of the NCEM, held in Brussels, Belgium, at the 29th and 30th of March 2017, presenting the main achievements of MODCOMP project in the field of carbon enhanced materials.



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Attending Graphene Week in Athens, Greece

GRAPHENE WEEK
25-29 SEPTEMBER 2017, ATHENS, GREECE

Originating from 2006, Graphene Week is an annual gathering for international leading experts on graphene and two-dimensional materials, creating Europe's most influential conference. Organised by the Graphene Flagship, the conference is set to present the latest scientific results, outstanding networking activities, and innovative exhibition opportunities.

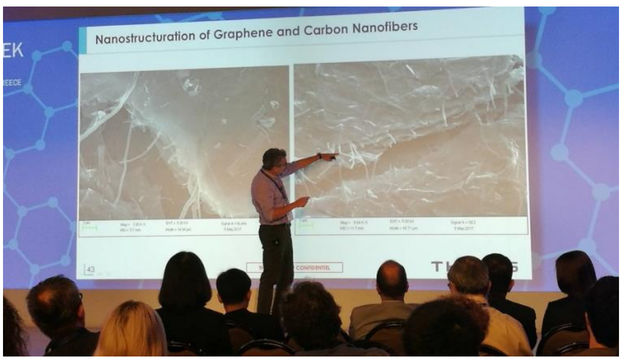
This year the Graphene week took place from 25th until 29th September 2017 in Athens, Greece.

Dr. Elias Koumoulos

NTUA participated in Graphene Week, in collaboration with THALES, presenting two posters.

Dr. Paolo Bondavalli

Dr. Paolo Bondavalli from THALES had two oral presentations with the title: "**Spray-gun deposition method of graphene and carbon based nanomaterials: history of an innovation"** and **"Graphene Based supercapacitors**".



Dr. Paolo Bondavalli

MODCOMP at the European Materials Research Society (E-MRS) 2017

The 2017 E-MRS Fall Meeting and Exhibit was held in Warsaw University of Technology, from September 18 to 20 (exhibition) and September 18 to 21 (technical sessions).

"The conference consisted of 23 parallel symposia with invited speakers, oral and poster presentations and a plenary session to provide an international forum for discussing recent advances in the field of materials science." was explained on their website.

Mr. Sergey Velychko and Mr. Igor Derevyanko

Yuzhnoye team participated with a presentation in conference. Mr. Sergey Velychko and Mr. Igor Derevyanko presented **"Experimental comparison of model cases of "cocoon", type from composite with and without surface modified Carbon Fibre"**.

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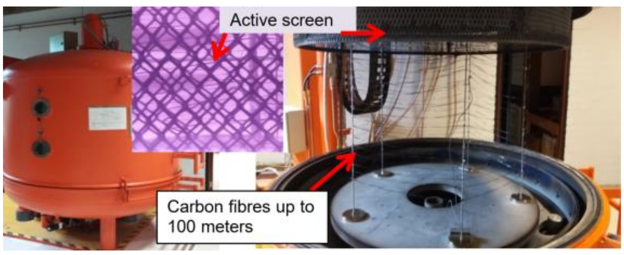
Recent Research Achievements

Surface modified multi-functional CNFs and CFs and optimal surface modification

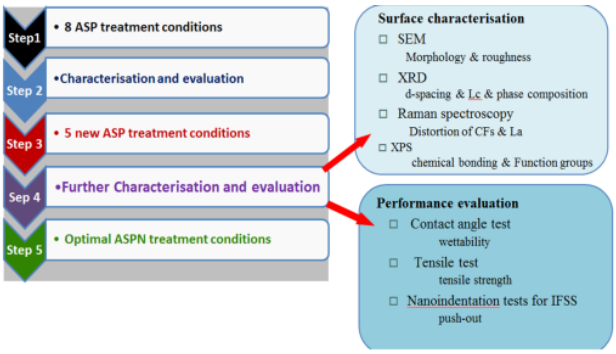
MODCOMP' aim is to develop surface modification procedures for multi-functional carbon nanofibres (CNFs) and carbon fibres (CFs) in order to enhance the adhesion strength between the fibres surface and the polymer matrix. Polito and UoB are dealing with plasma treatments while NTUA worked on electrochemical treatments.

Large quantity of surface modification treatments on carbon fibres have been taken out by (1) Politecnico di Torino (POLITO) and (2) The University of Birmingham (UOB) and (3) National Technical University of Athens (NTUA). Three different surface modification techniques have been developed respectively: Low-pressure plasma (LPP), Active-screen plasma (ASP) and Electrochemical treatment.



Setting up for active screen plasma treatment of the long length CFs

Large quantity of characterisation work has been carried out on the CFs in terms of surface morphology observation, Raman spectral analysis, XRD patterns identification, wettability measurements and tensile tests for strength evaluations. Schematics of the steps for ASP treatments are shown in picture below:

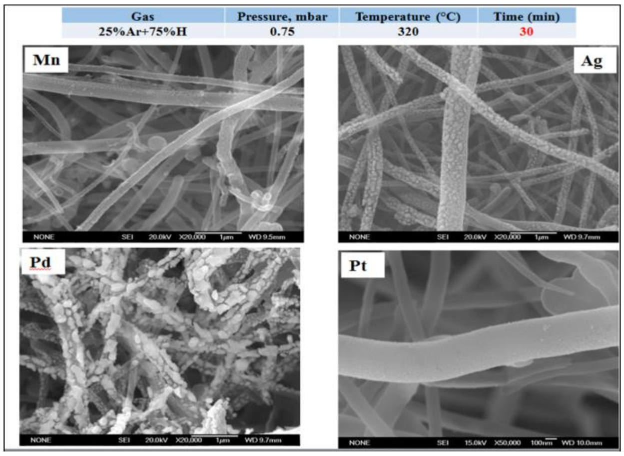


Schematics of the steps for the development of optimal ASP treatment conditions for CFs

Based on all the analysis results, the optimal treatment conditions for these three techniques have been identified:

1. For the LLP treatments, the 200W treatment condition performed an efficacy functionalization.
2. ASP treatments under conditions of ASPN5-0.75 and ASPAr5-0.75.
3. 15 cycles of treatment are the most optimum result for the electrochemical treatment modification.
4. For electro/polymerization, carbon fibres coated with PMAA have best wettability. However, by judging the sharp standard deviation of the contact angle the PMMA produced a homogenous coating on the fibres surface.

The metal additive ASP treatments were successfully applied to nano-carbon fibres. Picture below shows SEM images of the CNFs after ASP treatments with different metal additives. EDX analysis on the deposited CNFs revealed that the target material of Mn, Ag, Pd and Pt was deposited on the surface of the CNFs respectively.



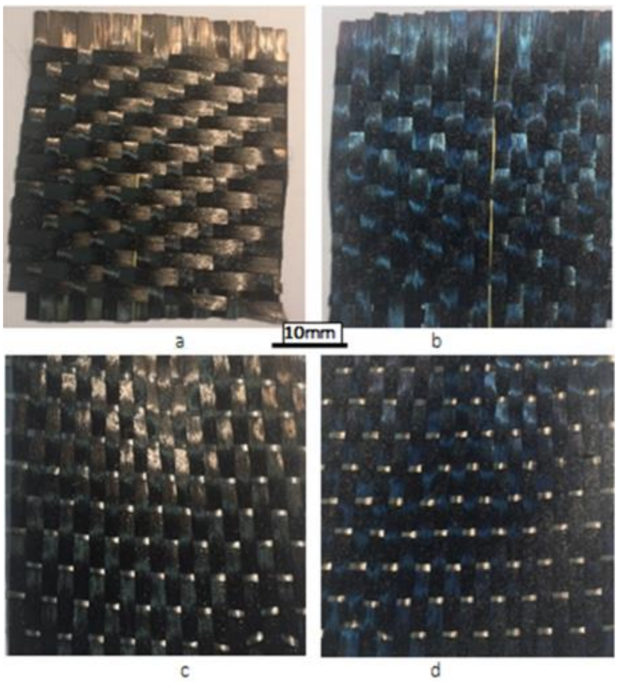
SEM images of CNFs deposited with Mn, Ag, Pd and Pt particles for 30 minutes, showing different surface features

Surface modified multi-functional carbon fibre woven structures

In order to facilitate the generation of high-performance 3D composites with excellent through-thickness properties, plasma surface treatment of woven CF fabric structures (G0926 and G1157) has been employed in terms of low pressure plasma (LPP), air pressure plasma (APP) and active screen plasma. The aim was to create a surface modification of the woven CF fabrics.

Analysis on these two woven structures CFs pristine and after plasma treatments were performed using FESEM/EDS, Raman. UoB performed also AFM surface observation.

Picture below shows the optical microstructures of G0926 and G1157 fabrics before and after ASP treatment. When fabrics were uncleaned, the colour of the fabrics changed to bluish after the ASP treatments. SEM observation found that the surfaces of the untreated carbon fibres changed surface morphology after the ASP treatment. The smooth surface of virgin HTA40 CF from G0926 fabrics show ASP treatment induced ripples and heaps.



Optical microstructures of G0926/G1157 fabrics a)/c) before and b)/d) after ASP treatment.

The characterisation of surface modified carbon fibres

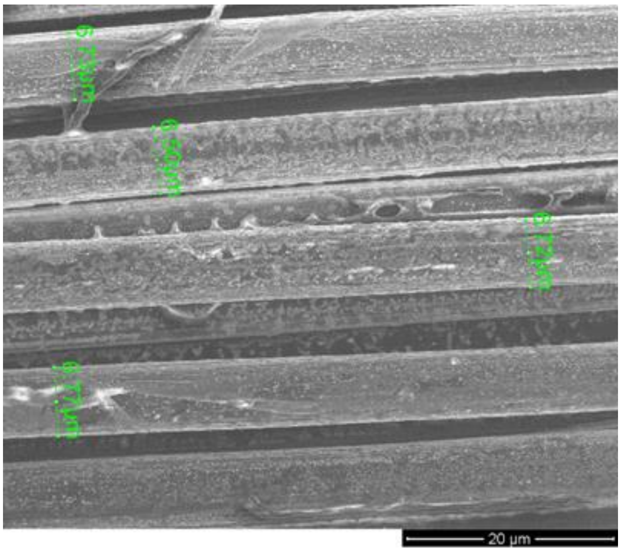
The characterization of surface modified carbon fibres aims to draw a comparison between each of the techniques used. This information will be used to draw conclusions about the effectiveness of surface modification and help to decide on the best method to proceed in carbon nanocomposite development.

A range of characterisation techniques have been employed by the project partners in order to gain an understanding of the changes taking place to the surface of the individual carbon fibre.

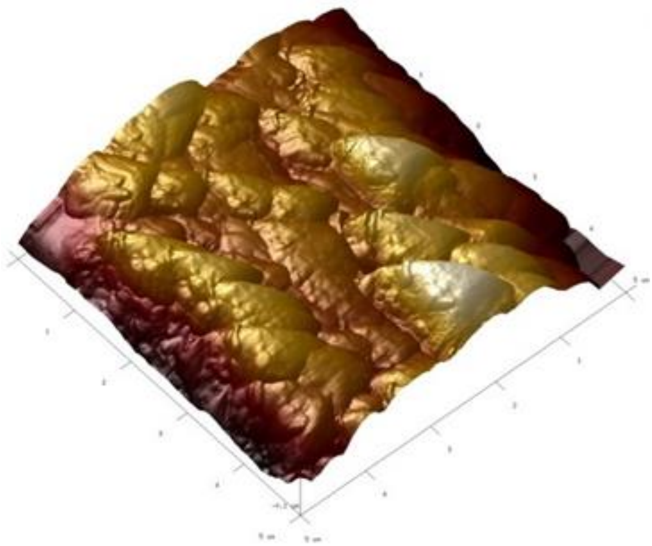
Optical micrograph of CF monofilament

<u>Optical Microscopy / Atomic Force Microscopy (AFM)/ Scanning Electron Microscopy (SEM).</u>

These techniques have enabled inspection of the impact on the various treatments on the surface of individual carbon fibres.



SEM image



3D AFM image of PMAA electropolymerised carbon fibre.
(Images courtesy of NTUA. TWI

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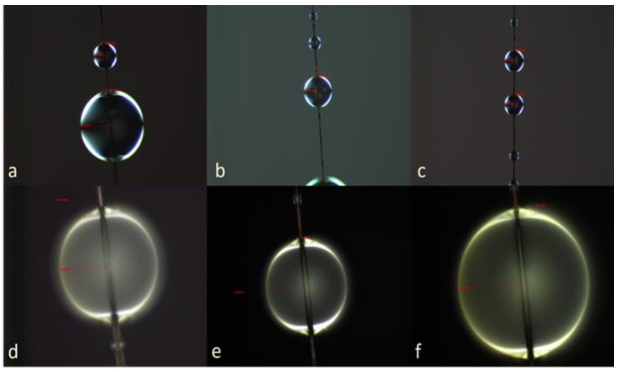
Other surface characterisation techniques have been employed, specifically, X-ray Diffraction spectroscopy (XRD), Raman spectroscopy andX-Ray Photoelectron Spectroscopy (XPS), to study changes on the surface of the carbon fibre via the different modification routes employed.

Wettability Measurements (Contact Angle measurements).

Different surface treatments will affect the surface energy of the fibre and ultimately how the fibres interact with the bulk resin.

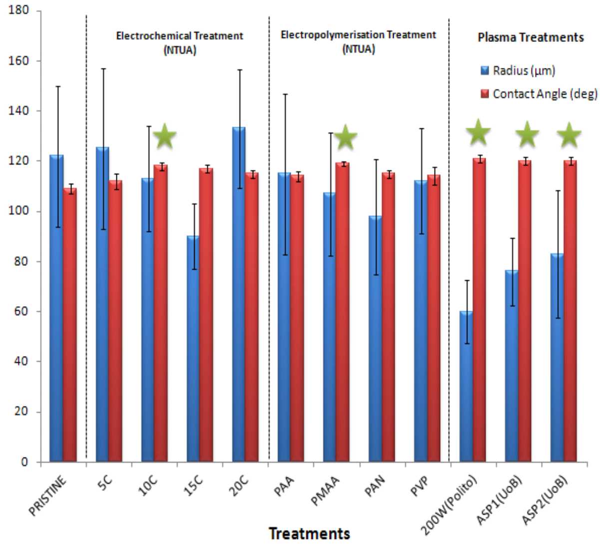
With contact angle measurements, we are able to assess whether the modified carbon fibres' wettability in epoxy resin has improved by wetting the fibres with epoxy resin droplets. After the fibres are wetted, optical microscopy and subsequent image processing is utilized to measure the outer or the inner contact angle. Increase in the outer contact angle can be interpreted as increase of the wetting properties of the modified fibres.



Modified Fibres after being wetted with epoxy resins, as seen in the optical microscope

The surface characterisation has highlighted a number of candidates whereby particular treatments can enhance the surface topography of the fibre.

- Electrochemical and electropolymerisation treatments exhibit the most obvious changes to the topography of individual carbon fibres.
- Plasma treatments contribute to bringing about improvements in wettability of the CF surface by Epoxy resin.



Contact angle (outer) analysis for all WP1 modifications, optimum results are highlighted in green

Deposition of CNTs/CNFs on CFs and CF fabrics via CVD

Two different approaches were tested so far for the optimal conditions of the deposition of Carbon Nanotubes on to Carbon Fibers, the floating catalyst approach and the supported catalyst approach; the results were characterized via SEM, TGA, and RAMAN measurements.

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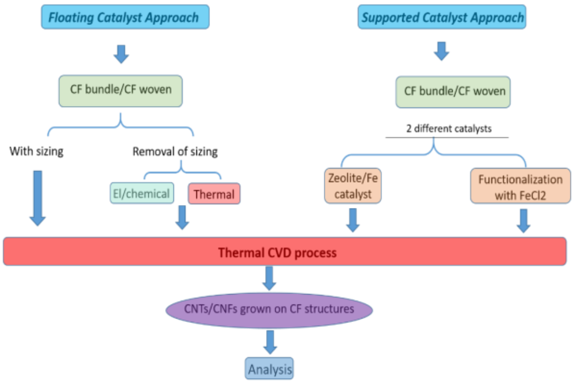
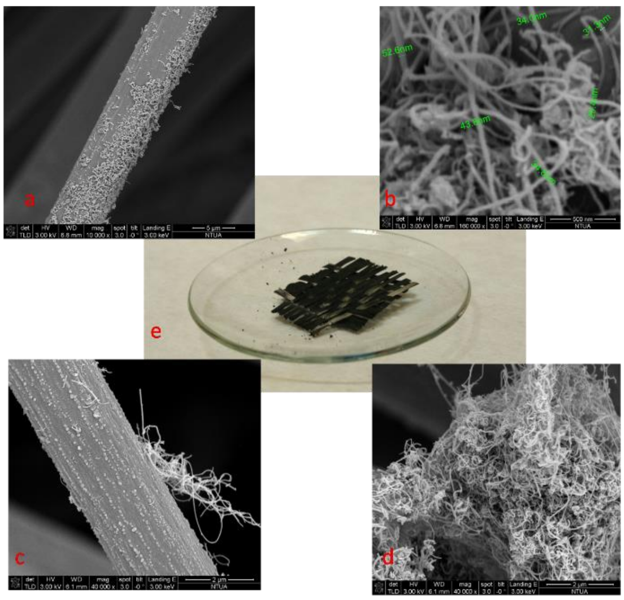


Experimental flowchart

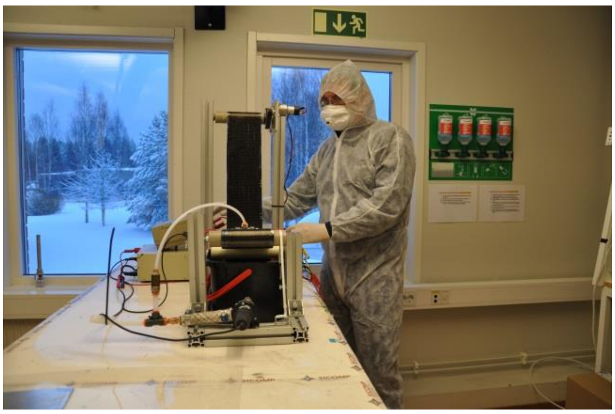
The supported catalyst approach, has proven to be the most promising procedure for the successful deposition of CNTs on CF fabrics in terms of morphology, quality of as grown CNTs, thermal stability, as well as the ability of the resulting structures to be further processed.



SEM images and macroscopic image of the Supported Catalyst experiment

Deposition of CNTs on CFs and CF fabrics via EPD

Electrophoretic deposition (EPD) is considered as a cost-effective method to coat substrate with conductive particles, such as carbon nanotubes (CNTs), with mild working conditions, requiring relatively simple equipment and being amenable to scaling up. However, it is hard to find any open report on coating carbon reinforcement with CNTs via EPD in a continuous process, revealing very low potential of being industrialized. A problem accompanied with the non-continuous EPD process is that CNT suspensions were discarded after each run of deposition, due to the absence of knowledge of measuring CNT concentrations during EPD process. This increases significantly the cost and generate serious burden to environment. In MODCOMP project, Swerea SICOMP, Sweden, designed, manufactured and verified a continuous EPD prototype that can be up-scaled for production of CNTs functionalized carbon reinforcement and resulting composites reaching TRL 5-6.



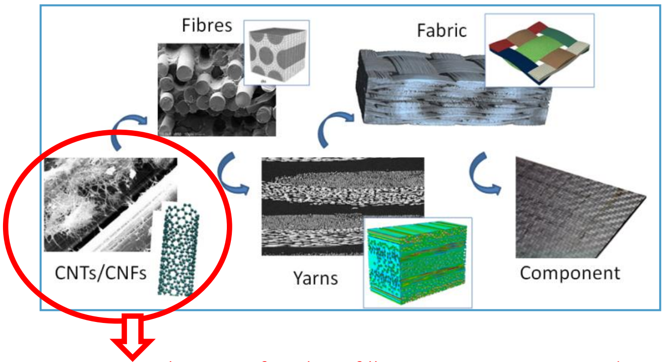
Operation of continuous EPD in the nanolab at Swerea SICOMP, Sweden

This prototype can be used for coating other conductive particles, such as graphene and metal nanoparticles, on different carbon reinforcement, fibres and fabrics. The prototype can be patented, and the patenting progress has been started in the IPR group at SICOMP. A methodology – modelling of nanoparticles concentration as a function of suspension viscosity was developed also at SICOMP to measure the concentration of CNT bath during the continuous EPD process. Accurate amount of fresh CNT suspension with well-defined concentration can thus be known to add into the EPD bath instead of discarding the whole EPD bath after each deposition operation. Unidirectional (UD) and cross-ply laminates where CNT coated carbon fabrics via EPD were impregnated by epoxy resin were successfully processed using resin transfer molding (RTM) technology. Much longer infusion time with coated fabrics compared to pristine fabrics and few CNTs observed in the resin at the outlet of RTM indicated that CNTs were coated through the continuous EPD process on the carbon fabrics without being rinsed by the resin under high pressure (3 bar).

UD laminates with 20 layers of CNT-coated carbon fabrics via EPD using 0.1 wt% MWCNT suspension from Nanocyl, Belgium

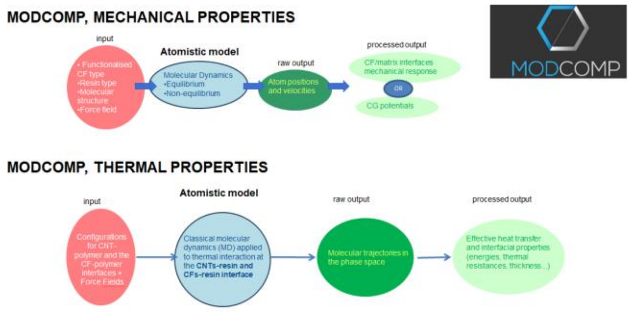
Molecular dynamics simulations

Molecular dynamics simulations of carbon fillers, resin matrices and nano-composites are also the focus on the project. Modelling at atomistic level was the challenge. These models constitute the first level of material structure description within the multi-scale approach proposed.

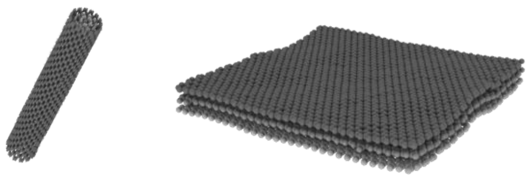


MD simulations of carbon fillers, resin matrices and nano-composites

These models constitute also the starting points of the workflows for thermal properties and mechanical properties (both case #1 and case #2), described according to the MODA (MOdelling DAta) approach recommended by the European Materials Modelling Council (EMMC, https://emmc.info/).

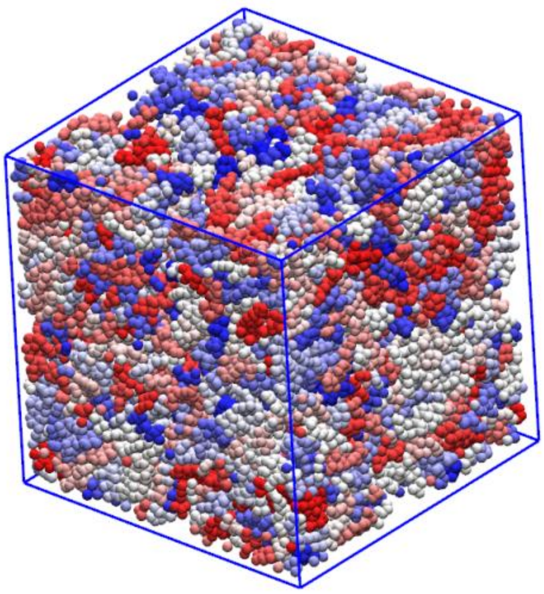


MD models have been developed to study the properties of CNTs and graphene fillers considering different parameters (as length and diameter). This allows obtaining effective properties of these reinforcements (needed for the models proposed in MODCOMP in other scales, bottom up approach).



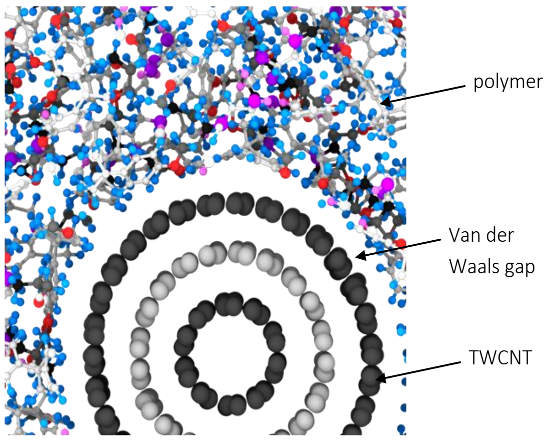
MD models of CNTs and graphene layers studied in MODCOMP

In addition, MD models have been prepared to characterize the thermal and mechanical properties of some of the polymer matrices selected in MODCOMP.

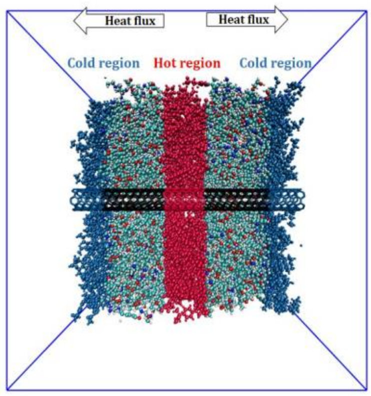


Simulation box prepared to study one of the epoxy polymers selected in MODCOMP

Finally, the activities performed have allowed i) determining of CNTs/CFs/GS/GNRs-resin interfaces properties (again, needed for simulations in larger scales) and ii) obtaining effective mechanical and thermal properties of some selected materials systems to evaluate the effect of the CNTs as reinforcements (alone or deposited on CFs). Mechanical properties as the elastic constants and the interfacial shear strength (IFSS) and thermal properties as the thermal conductivities and the Kapitza resistances have been studied. The effect of various geometrical parameters, such as length and diameter of fillers, or chemical factors, such as degree of cross-linking, has been investigated to see how the final properties of composites can be controlled by modifying the atomistic characteristics of their components.



Detail of CNT/epoxy the interface region



MD study of thermal response in a nano-composite

Development of process simulation

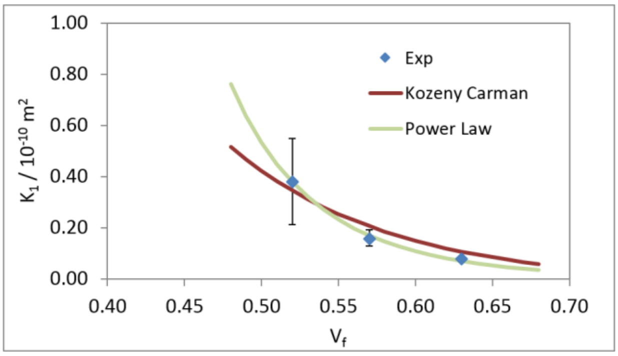
Numerical simulations can aid the cost-effective optimisation of manufacturing processes. This is true for any process and material, but especially for expensive materials such as polymer composites. This work aims to demonstrate the development stages and a methodology to be followed when developing resin flow and cure simulations for the resin transfer moulding (RTM) manufacturing process as a sub-set of liquid composite moulding (LCM) manufacturing processes.

The numerical simulation of liquid composite moulding manufacturing processes require:

1. material characterisation generating robust input datasets,
2. reliable modelling tools,
3. expertise availability.

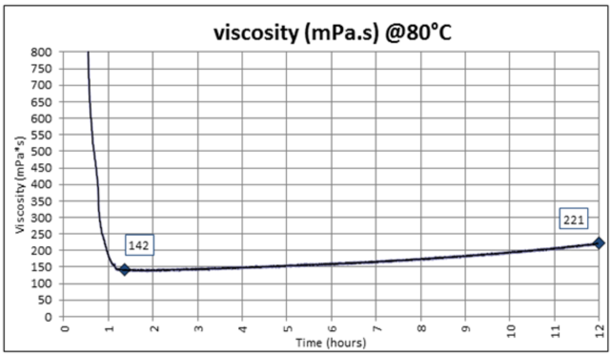
However the technology readiness level (TRL) of the overall predictive technology for liquid composite moulding, inclusive of points 1), 2) and 3), is lower than the current TRL level of LCM manufacturing process.

The fluid flow through a porous media is modelled using Darcy's law. The permeability of the carbon fibre material is a key parameter that needs to be characterised. In-plane and through-thickness permeability values are obtained for a selection of fibre volume fractions of the final part and this data is used to interpolate permeability values for a range of fibre volume fractions. This is a non-trivial task as a standard is not yet developed for permeability characterization.



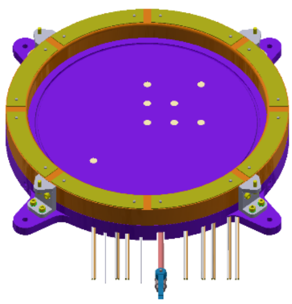
Reinforcement characterisation

The variation of the resin's viscosity with temperature and its development with time is measured experimentally for the simulation of flow.



Resin characterisation

A series of panels were moulded at the NCC, to serve as validation for the numerical simulations. Sensors were placed in the mould in pre-determined positions in order to record resin arrival times and degree of cure against time during the cure cycle.



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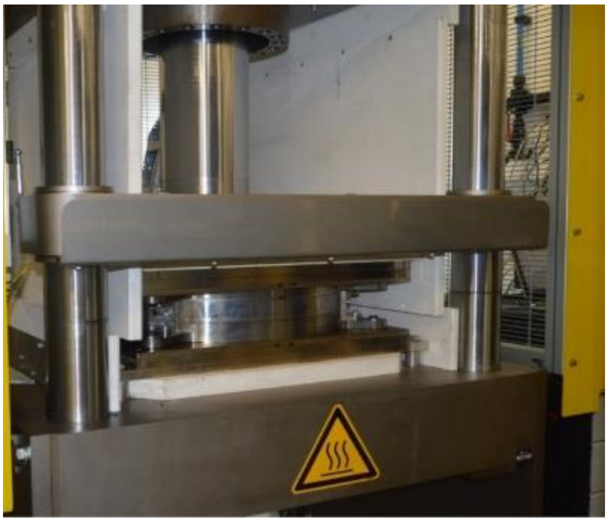
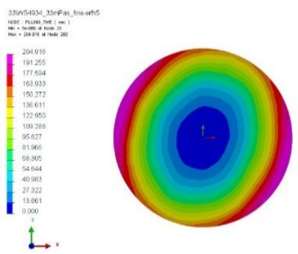
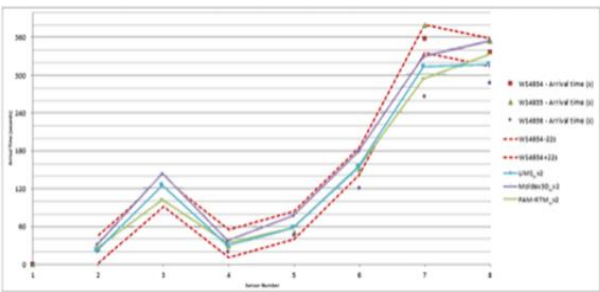


Manufacturing Trials



Flow and cure simulation models were developed and run, and their predictions compared against experimental results. Comparisons between simulation and experiments for flow arrival times and degree of cure development with time showed promising degrees of correspondence.

Developed resin cure kinetic models are used for the simulation of the curing process. Resin cure modelling and characterisation is currently at a relatively high technology readiness level and can be used industrially.

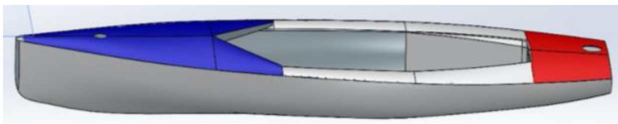


Simulation

Prototype moulds

There are three of the demonstrators planned within the MODCOMP project. The “SleekFast” prototype moulds, the “AdShel” prototye moulds and “SecureShel” prototype moulds.

The progress on “SleekFast” prototype is progressing towards the plan. The hull form was made using foam, wood, glass fibres, resin, various fillers and plenty of sanding so that the surface was smooth and ready for painting.



The model of the hull

The hull form was then painted with various layers of polyurethane high gloss paint. Hull and deck moulds were constructed in glass fibres (roving and mat) polyester resin isophtalic gel coat and using hand lay with vacuum bagging.

In the next phase we will refine the prototypes and we will continue and carry out sea trials.

Advanced Material Shelter System - “AdShel” Shelter System is in the phase of creating the form using traditional mould making skills. The basic form, created using melamine board, dressed timber and flexible sheet material, measured and checked for accuracy against the CAD drawings was made.

AdShel unit

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In the next phase we will refine the prototypes and start to develop metal fixings and install window apertures.

For the “SecureShel” prototype, the flat panel forms were created using traditional mould making skills. Materials used were melamine board and flexible hard board strips.
After using mould putty to fill any imperfections in the forms, five coats of mirror glaze release wax were applied.
In the next phase the prototypes will be refined, metal fixings the hydraulic / pneumatically assisted folding mechanism.

Risk and Safety Assessment

The extended use of CFs in both research and industrial environments has set the demand for the establishment of safety rules for handling the carbon-based materials.

The goal is to examine and gather all the health and environment risks posed by the use of CFs and hence put safety concerns in perspective. In this context, IRES team created a Risk & Safety Assessment flyer in order to facilitate the estimation of any potential hazard, arising from the use of Carbon-based materials and Carbon-based engineered Nanomaterials, and the identification of those things, situations and processes that may cause harm, particularly to people and the environment. The leaflet includes all the necessary information to enable MODCOMP partners to decide whether they have taken enough precautions or they should do more to prevent any possible harm.

Possible exploitation routes in the market

A competitive intelligence study

A competitive intelligence study has been started by Brembo and OSM. Competitors, customers and potential partner profiles were analyzed with the purpose to define their positioning in the market and therefore better target the exploitation strategy implemented for the whole duration of the project from all partners.

BMW Carbon core structure (source: BMW)

This preliminary study has been dedicated to three specific areas: automotive, aerospace, and renewable energy; in the next months, more technologies will be included.

BMW HP4 Race Carbon Fiber frame (source: BMW)

Automotive applications of CF reinforced composites and plastics (CFRP) are increasing either for body or chassis components. BMW, Mercedes-Benz, WV-Audi (Lamborghini) and other automakers have committed to the increased use of CFRP components in their vehicles to reduce weight, save fuel consumption and save GHG emissions. In the motorcycle business, BMW HP4-Race was the first stock motorcycle in the world to have fully carbon chassis and rims. Ducati has also presented the 1299 Superleggera, where lightweight carbon fibre wheels debut on a production motorcycle and greatly reduce unsprung rotating mass, ensuring agility while maintaining maximum resilience. In a recent forecast concerning carbon fiber for automotive application, IHS experts outlined growth of almost 9% by 2020.

Aerospace market for CFs composites is driven by the significant weight and performance (high stiffness) advantages. B787 and A380 aircraft, over 250 tons jumbo jets, use CF composites in almost 50% of the aircraft in weight and 80% composite by volume. Large-scale commercial aviation aircrafts market is expected to yield around 12500 new aircrafts in the next ten years (Airbus Global Market Forecast 2010-2029, 2010). Boeing is forecasting for 30,900 new civil aviation aircraft for the period 2010-2029 with a market value of 3,6 trillion $ (Boeing Current Market Outlook 2010 to 2029, 2010).

According to latest studies, Wind energy sector should represent 60% of carbon fiber consumption of global market. This sector consumed 15,000 tonnes of carbon fibres in 2012 and could reach 37,000 tonnes in 2020.

A350 XWB benefits from being built with over 70 per cent advanced materials, combining carbon composites up to 53 per cent (source: Airbus).

Vestas has installed more than 1300 offshore blades that incorporates carbon fiber core (source: Vestas wind systems).

The market forces that drive carbon fiber supply and demand are numerous and complicated. It's evident, however, that a few indicators, with little change, have the capacity to substantially shift the carbon fiber market.

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