KETmaritime Case Study 2 – Nanotechnology Marine Applications

A pioneering scientific centre in northern Portugal has led a major two-year project studying advanced manufacturing technologies with the potential to revolutionise the Atlantic maritime sector. The International Iberian Nanotechnology Laboratory (INL) located in Braga is the lead partner in the €1million 'KETmaritime' project backed by the European Regional Development Fund. Project coordinator Ana Vila said the INL is now releasing details of a second case study focusing on 'Nanotechnology Marine Applications'. She said the pan-European project identifies how advances in this field will be of benefit to the shipbuilding, ship maintenance, oil & gas, fuel additive, aquaculture and fishing markets.

Key findings from the KETmaritime project are now being revealed following two years of intensive international work involving a world-class consortium of partners across Spain, Portugal, France, Ireland and the UK. Its mission is focused on identifying KET (Key Enabling Technologies) to meet the future needs and demands of the Atlantic maritime industry.

Project partners include French multidisciplinary research laboratory CIMAP (CEA group), Portuguese maritime economy association Fórum Oceano and Spanish technology centre IDONIAL. Ireland's national centre for marine and renewable energy MaREI, UK marine cluster organisation Marine South East and Spanish technology centre AIMEN complete the consortium.

A total of five detailed case studies have been produced under the €1million initiative. Topics include 'Advanced Manufacturing Shipbuilding Applications', 'Nanotechnology Marine Applications', 'Marine Industrial Biotechnology', 'Photonic Marine Applications' and 'MEMS (Micro Electromechanical Systems) Marine Applications'.

Nanotechnology – manipulating matter at the atomic scale

The second case study led Spanish technology centre IDONIAL in collaboration with Marine South East in the UK focuses on 'Nanotechnology Marine Applications' (access http://ketmaritime.eu/media/ to view the full report). In addition, the International Iberian Nanotechnology Laboratory (INL) provided key input. The INL was created by the Portuguese and Spanish governments as a world-wide hub for the deployment of nanotechnology addressing society's grand challenges.

The detailed report illustrates the growing interest in this pioneering form of technology which approaches products and processes from the smallest achievable physical scale. 'Nanotechnology' or 'Nanoscience' is a broad concept. It covers the design, characterization, production and application of structures, devices and systems by controlling shape and size at a molecular or atomic scale. The size of this 'working zone' is usually defined as between 1 and 100nm. Sizes in which the matter begins to manifest unique behaviours compared to those witnessed in classical mechanics, leading to the so-called 'quantum effect'.

At these scales the behaviour of matter can vary and in some cases it differs greatly from what is observed at non-nanometer scale. For example, at nanometer scales the melting points of metals such as gold and silver are greatly reduced compared to 'macro' form melting points which are above 1000C. The limit is greatly reduced by hundreds of degrees when the diameter falls below 20nm. These variations are largely the result of increased surface area. As particle size decreases the material is exposed to energy sources and other materials to a greater extent, increasing its reactivity and even turning non-toxic macro scale materials into toxic materials. In the same sense other properties can be modified including conductivity and colour.

The term 'nanomaterial' is used to describe objects in which at least one of its dimensions has a nanometric scale (1-100 nm). Material with 3 nanometric scale dimensions include nanoparticles, quantum dots, nanoshells, nanorings, nanocapsules. Those with 2 nanometric scale dimensions include nanotubes, nanowires, fibers. Other such as films, layers and coatings have 1 nanometric scale dimension. In most applications we identify 'nanomaterial' as additives or elements implemented within standard materials. For example, they can be incorporated with metals or alloys, composites, coatings, polymers, semiconductors and ceramics to achieve a certain function or capacity.

Nanotechnology – small scale technology with far reaching effects

Nanotechnology is applicable in a large number of disciplines, but its general applications can be condensed in the following areas – Material Science, Medicine & Health, Food & Nutrition, Electronics, Energy, Environment and Information Communication Technology.

Within 'Material Science' work at the nanometric scale enables deeper investigation around characteristics and phenomena giving rise to the properties of a given material. This is ultimately the basis for generating materials with improved characteristics. It can lead to the development of materials in the form of nanoparticles, nanofilms, or others, which in turn influences the development of materials and coatings with 'smart' behaviour, interacting in a unique way compared to materials engineered at 'macro' levels.

In the 'Medicine & Health' sector the application of nanoparticles can be summarized in four large groups. This includes 'Diagnosis' through the use of nanosensors based around the development of miniaturized 'in-vitro' devices for the detection of nanoparticles and nanostructures. Secondly, 'Imaging' uses nanoparticulate compounds as contrasts to carry out tests for the detection of diseases. Thirdly, 'Therapy' harnesses nanotechnology for the design and development of substances and drugs with very specific effects. Lastly, 'Regenerative Medicine' uses nanotechnology for the production of nanostructured scaffolds for the growth of organic tissues, as similar as possible to natural tissue.

Within 'Food and Nutrition' nanotechnology has applications at various levels. It is used in agriculture to produce nanosensors for the detection of pathogens, and nanoparticles for the supply of pesticides and other products. In broader food processing nanoparticulate additives are used for the improvement of organoleptic properties and general conservation. Furthermore, within food packaging nanosensors are used to control food characteristics, while the development of food supplements contains nanoparticulate nutrients.

Scientists have also been progressively using nanotechnology to miniaturize components for the 'Electronic' sector. This has given rise to chips and processors capable of housing large quantities of transistors in very small spaces. A move which has driven the enormous development of mobile technologies in the 21st century. It has also influenced additional advances in fields such as roll-up and flexible electronics, and high-resolution screens. However, nanotechnology has many other applications in this field including the development of data storage systems, wireless communication systems, wearables and electronic paper.

There are also numerous fields nanotechnology can be harnessed to improve the performance of existing 'Energy' applications. Key areas include the improvement of catalysis of fossil fuels and the performance of renewable energies through the design of lightened elements, such as superconducting materials.

It offers further solutions for the 'Environment'. There are several pollutants which are highly harmful even in the low concentrations - such as mercury where the toxicity threshold is only 1 or 2 parts per million. Nanotechnology is a hugely effective tool for detecting and treating these pollutants in the same way it can be applied to the development of coatings specifically designed to counteract contaminants or prevent their deposition.

Finally, there are a multitude of ways in which nanotechnology can be applied to the marine sector and maritime environments. Key areas of interest include nanocoatings protecting against corrosion and biofouling on ships, as well as new materials for shipbuilding and a variety of uses across Oil & Gas Industries. The technology is also being used to advance the development of fuel additives, alternative powering systems, aquaculture and fisheries.

Nanocoatings for vessels – total protection against corrosion and biofouling

Corrosion and biofouling are two of the largest challenges affecting material exposed to harsh marine conditions reducing both durability and performance. In the case of corrosion, the deterioration process is caused by the alteration of a metallic material as a result of an electrochemical attack. This leads to a progressive process of oxidation essentially altering its basic nature, and ultimately destroying it, putting the integrity of the material in danger. The process occurs naturally with almost all untreated metallic materials. However, the process is accelerated in the marine environment where humidity and salinity levels are estimated to be the cause of approximately 30pc of all vessel failures, repair needs and equipment malfunction. This degradation process comes at a considerable cost to marine operators in terms of maintenance and repair activities.

Biofouling, meanwhile, is a process by which microorganisms accumulate on a material. In cases involving widespread biofouling, the organic mass can modify the shape and hydrodynamic behaviour of a given material. This is especially undesirable in maritime transport applications, where high levels of biofouling can increase water resistance and fuel consumption. This phenomenon again occurs naturally within minutes on any surface being submerged as organic matter dissolved in seawater begins to settle, forming a light film (microfouling), which progressively evolves into larger 'colonies'.

The most commonly used solutions to protect against corrosion and biofouling involve coatings and paints, temporarily protecting structures from degradation and improving aesthetics. In the case of marine applications, certain coatings have been specially engineered to provide superior and durable protecting effects for submerged surfaces. Not only does this provide protection it also enhances performance and reduces fuel consumption. In recent years there have been huge improvements in the durability of materials subjected to the marine environment, due to intense study and development. However, both phenomena continue to present highly relevant problems to which mitigation and solutions are continually being sought.

Organic polymeric coatings are now widely used to protect against corrosion due to reasonable costs. These coatings include inorganic particles or passivating compounds that act as corrosion retarders or 'barriers' preventing direct contact between the surrounding media and the metal. However, these 'barriers' are not able to provide total coverage, as the coatings contain pores which aggressive ions are able to penetrate. This starts a corrosion process that can lead to a significative alteration of the surface. In the case of antifouling coatings, Self-Polishing Copolymer (SPC) antifouling paints are predominant. These are engineered to slowly release biocides that essentially prevent the deposition and growth of marine life over surfaces. However, due to their very nature these forms of anti-fouling coatings consume themselves over time, ultimately presenting the same problem it was initially designed to reverse. From an environmental perspective, the release of biocides which poison the marine environment also give rise to concern.

The key reason corrosion and biofouling continue to pose challenge is because so far both the materials and their manufacturing and treatment processes present defects. Although small, these defects favour both the oxidation processes and the accumulation of biomass. A new solution being explored is the development of 'nanostructured' coatings using 'nanoparticulate' substances. These coatings are capable of providing considerably superior protection compared to traditional coatings, based on the use of substances capable of forming and interacting on previously unreachable (nanometric) scales, in which the corrosion phenomena and biofouling begin.

In the field of anti-corrosion, there are now numerous companies developing specialised nanotech products to prevent or avoid corrosion. In all cases the operation of these coatings is based on the principle of generating a uniform low surface energy at nanometric scale, in order to reduce reactivity to sea water, thus avoiding the unwanted oxidation processes. Current products include nanoadditives such as nano-ZnO, nanoalumina, nanosilica. One reason why nanotechnology is being proposed as a solution to biofouling is because of its environmental benefits. At nanometric scale biocidal compounds can be bonded to the surface strongly. When combined with non-stick antifouling coatings biocidal action only occurs in the event of direct contact with marine organisms. The capabilities of this technology are still being explored with similar strategies applied to the corrosion issue. Thanks to nanotechnology it is possible to maximize the anti-adherent or repulsive capabilities of a surface, and therefore eliminate the need to use biocides.

Nanotechnology in Shipbuilding – reducing weight and driving operational efficiency

As with any application requiring considerable amounts of construction material one of the most critical aspects is the minimization of weight while maintaining both resistance and performance. This is doubly critical for the shipbuilding process if we take into account the potential to drive manufacturing savings while slashing down on the consumption and impact of vessels. One of the main areas in which nanotechnology is providing tangible solutions is composites, where nanometric structures are improving materials. The implementation of carbon nanotubes in composites, in conjunction with mature materials such as carbon fibre, is significantly increasing strength, doubling or even tripling the values of conventional carbon fibres – without increasing weight.

This method has been proven by Zivex Technologies, based in Ohio, USA, which in 2010 built an unmanned surface vessel for the US Navy codenamed ‘Piranha’. This vessel used nanotube-reinforced fibre composites. Furthermore, in 2017, Spanish company Graphenano presented the first Spanish boat using graphene technology in the construction process. In both cases, designers declared that nanomaterials were the catalyst for significantly surpassing the performance of traditional materials, leading to lighter vessels. In the case of Zyvex´s Piranha, a 75pc weight reduction was recorded in comparison to the traditional fiberglass ship. Meanwhile, Graphenano´s vessel saw a 20pc weight reduction, with a direct impact on fuel consumption, costs and environmental impacts during planned lifetimes.

The influence of nanotechnology in shipbuilding is becoming increasingly prevalent particularly in the field of composites. Vessels such as pleasure boats and high-performance vessels which heavily use composite materials are likely to witness more rapid change. Meanwhile, the implementation of nanostructured materials in larger vessels is expected to increase as systems for the application of composites on structural elements are further developed.

Nanotechnology for Oil & Gas Industries

Nanotechnology offers widespread benefits to the oil and gas industry. In a similar respect to the shipbuilding sector it offers major benefits in coatings and structural elements. It also presents opportunities to the oil and gas industry as a concrete additive, drilling stabiliser and water treatment solution.

The field of coatings is perhaps where nanotechnology is already providing more tangible results than anywhere else. Specific products are now being developed which incorporate better anticorrosive properties and barriers against biofouling than any traditional solution. The advantages described in the previous corrosion and biofouling section are also directly applicable to the field of oil and gas. Various nanostructured materials are also being investigated as additives for concrete. In particular, Nanosilica, nano-Fe2O3, carbon nanotubes and nanoalumin are being intensively tested in order to improve resistance to bending and compression of Portland and Belite cements, while also presenting other qualities of interest as a self-monitoring capability.

A series of interesting applications are emerging regarding the use of nanomodified steel. One of the most high-profile examples has been developed by MMFX Technologies which produces MMFX2 - a nanomodified uncoated corrosion-resistant and high-strength reinforcing steel. This product consists of reinforcement bars for concrete structures offering anticorrosive properties derived precisely from its nanostructure. Meanwhile, nanomaterials can play important roles in the efficiency and safe performance of drilling activities. In particular, they can play an important role in stabilization tasks and reducing losses in wells, where nanostructured elements are able to penetrate the smallest pores. This type of additive can drive the performance of operations, based on an improvement in the rheology of the fluids used for drilling and an increase in their thermal stability.

The oil and gas industry is especially intensive in the use of water which is demanded in drilling operations and oil refineries. It is also responsible for heavily polluting water systems. Nanostructured materials can be used within filtering operations prior to the return of water to the environment. The technology would drive performance by reducing the cost of conditioning operations, based again on a larger specific surface, with a greater ability to retain contaminants compared to traditional filtering materials.

Fuel Additives and Alternative Powering Systems

Despite the evolution of renewable energy, and the development of electric engines, traditional fuels continue to have and will maintain a vital role in marine activities. However, given its impact on the environment, we have witnessed a progressive development in both combustion systems and fuels themselves, now being used in an increasingly efficient way. Various additives are being investigated as a way to obtain more efficient fuels with a reduced impact on the environment. For example, metallic oxides have been used as fuel additives in yachting, reducing exhaust soot and diesel engine consumption through the addition of cerium oxide nanoparticles. This was tested as early as 2011, when Cerion Energy produced its GO2 Diesel Fuel Optimizer and installed it on two superyachts - Big Fish, a 45m expedition-style yacht and Apogee, a 62m motor yacht. Both cases produced a 10pc improvement in fuel economy.

In terms of new powering systems, there has been significative improvement in battery chemistry combined with use of cleaner fuels as the size of vessels increases. Nanotechnology is further expected to bring a quantitative leap, as nanostructured batteries and electrodes offer considerably improved performance.

Developing and optimising aquaculture and fishing activities

Nanotechnology is currently one of the main tools being used to develop and optimize aquaculture and fishing activities. Applications range from the use of nanobiosensors for the control of toxic substances in water to the identification/ tagging marine species. Further significant developments include the use nanoparticles as food supplements, vaccines, proteins and the purification and filtering of water.

Nanobiosensors are now being used heavily in aquaculture activities to control substances in the environment for fish growth and critically to ensure a high survival rate free of toxic elements. For example, gold nanoparticles are used for the detection of chemical contaminants. Gold nanoparticles are particularly well equipped for the detection of substances, due to their surface electrons which are highly sensitive to changes in surroundings. These nanoparticles have also been successfully used to detect heavy metals, aromatics, nitrates and toxins of natural origin. In addition, Nanosensors are deployed for the detection of methylmercury – which is particularly dangerous for organisms due to its toxicity and cumulative effects. In 2014 researchers from the University of Vigo developed a nanosensor which measures this compound in fish and shellfish in situ, without the need for a laboratory or instrumentation on land. In this regard nanosensors are highly effective as part of an early warning network for toxins and pollutants. The development of these technologies can be found in the Enviguard project (7th Framework Program, 2013-2018) which saw the development of an early warning system for aquaculture and environmental control activities. One of its sensor systems consisted of a nanobiosensor for the detection of chemical substances and toxins.

Nanoparticles are also highly effective in the administration of nutrients and substances to ensure growth free disorders across fish stocks. In 2003 the Russian academy of sciences showed how the presence of iron nanoparticles favoured the growth of carp and sturgeon, increasing growth rate by more than 20pc. Iron is an indispensable element in the development of organisms, playing an important role in many processes including oxygen transport. Similar studies involving the use of zinc oxide nanoparticles in combination with immune-stimulant ß-glucan binding proteins within fish diets led to increased growth and survival rates. Meanwhile, nanotechnology is also being used in the fish vaccination process where antibiotics prove inefficient. Vaccination techniques include the use of antigens housed in nanoparticulate materials. Another possible use includes water treatment to avoid fungal infections. This involves the use of silver nanoparticles as coatings in water filters, preventing fungal infections in rainbow trout fish.

Advances in miniaturization technologies, currently commercially reaching the 7-nanometer border, have made it possible to manufacture very small size chips with identification and location functions. This enables the monitoring and analysis of the evolution of a certain fish population, whether in open water or from aquaculture, or the tracking of the fish after catching up to its final delivery. Small radio transmitters have been used for several years to collect data from marine species. Organisations including Lotek Wireless in Canada have been developing and distributing this form of technology and it can be expected that progressive miniaturization will bring new possibilities and more efficient identification and tagging techniques.

For more information on the KETmaritime project visit the website www.ketmaritime.eu phone +351 253 140 112 email Ana Vila on Ana.Vila@inl.int

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Project Partners:

Notes to editors:

Interreg
Atlantic Area
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KETmaritime

KETmaritime is a €1million project that aims to transfer Key Enabling Technologies (KETs) to the Maritime Industries of the Atlantic Area. Focused on building a cooperative network that stimulates innovation and competitiveness, the project embraces the challenge of increasing the capabilities, skills and knowledge on KETs in an integrated and cross-national approach. The consortium brings together seven partners from five countries that, under the framework of the project, work closely with industries and businesses. The ultimate goal is to bring to market new processes, products and services. Partners in the consortium include French multidisciplinary research laboratory CIMAP (CEA group), Portuguese maritime economy cluster Fórum Oceano and Spanish industrial design centre IDONIAL. Ireland’s national centre for marine and renewable energy MaREI and UK marine cluster organisation Marine South East are delivering further support, alongside Spanish non-profit research association AIMEN. KETmaritime is a project funded by the Interreg Atlantic Area Program, supported by the European Regional Development Fund.