Novel antifouling coating containing biocide functionalized silica nanoparticles in a polyurethane matrix for tidal blades

September 13th 2022

FUNDITEC

tecnalia
MEMBER OF BASQUE RESEARCH & TECHNOLOGY ALLIANCE

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Coordinator of NEMMO H2020 project (GA #815278)

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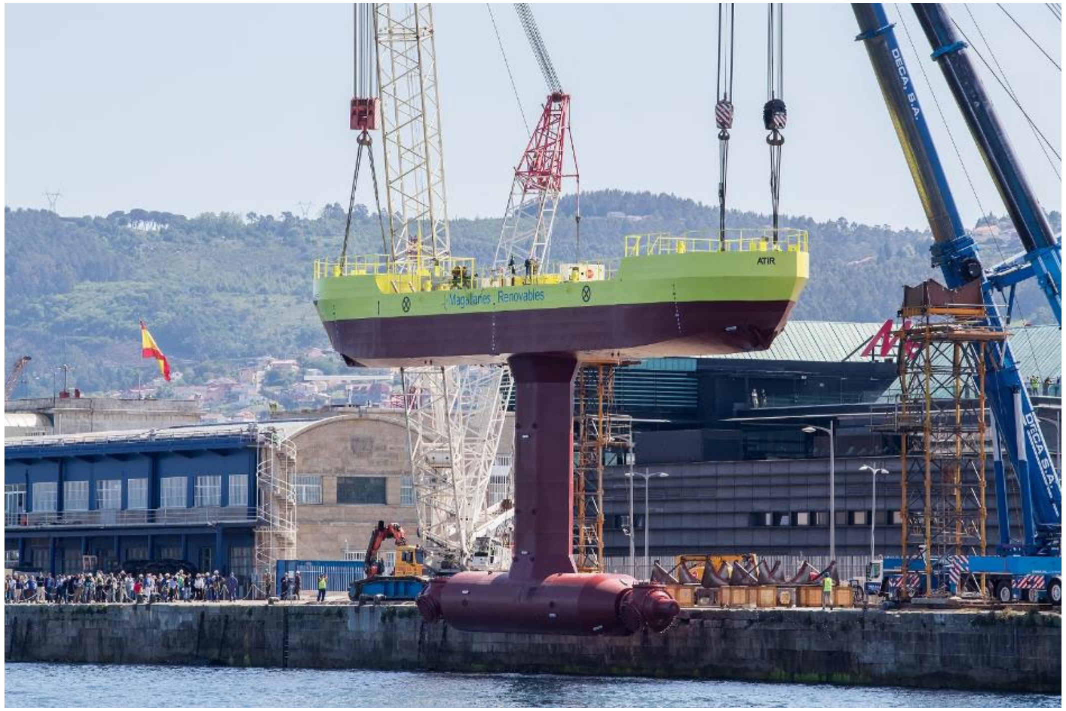
Objective

The H2020 ***NEMMO*** *project seeks to generate novel* ***models, knowledge, designs*** *and* ***testing procedures*** *to develop* ***more efficient composite TIDAL TURBINE BLADES*** *and thus lower the LCOE of tidal energy****.***

Very specific conditions due to ***tide cycles***



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Objective

New materials for blades in NEMMO project:

Blade Composite

- Nano-enhanced material for higher fatigue and resistance composite

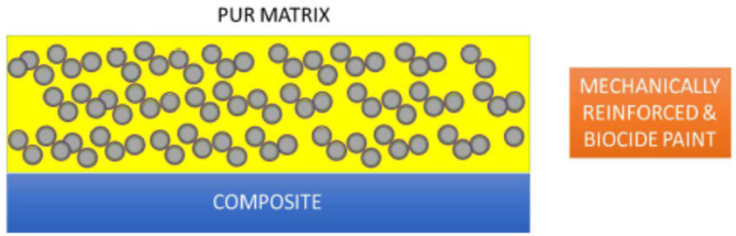
Biomimetic surfaces

- Mimicking brill fish skin with antifouling properties
- Laser micro texturing

Blade Coating

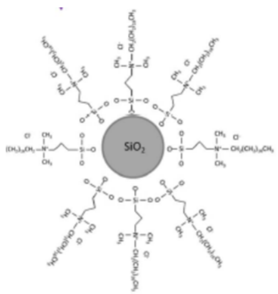
- Increased non-leaching fouling resistance
- Metal-like cavitation resistance

1. Synthesis of permanent cavitation resistance, non-leaching anti-fouling coatings

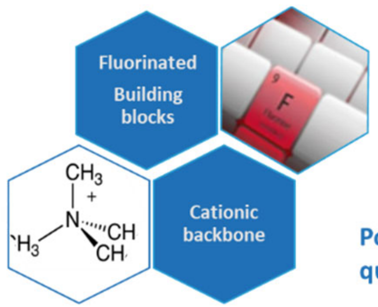


A two steps approach was designed:

1. Include biocide functionalised silica **nanoparticles**



2. Design of highly crosslinked polyurethane dispersions (PUD) containing cationic copolymers and NP for cavitation and antifouling resistance



Decreasing surface energy

Positively charged ammonium quaternary salts

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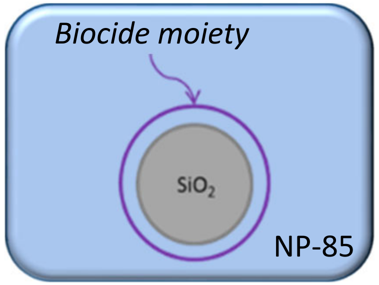
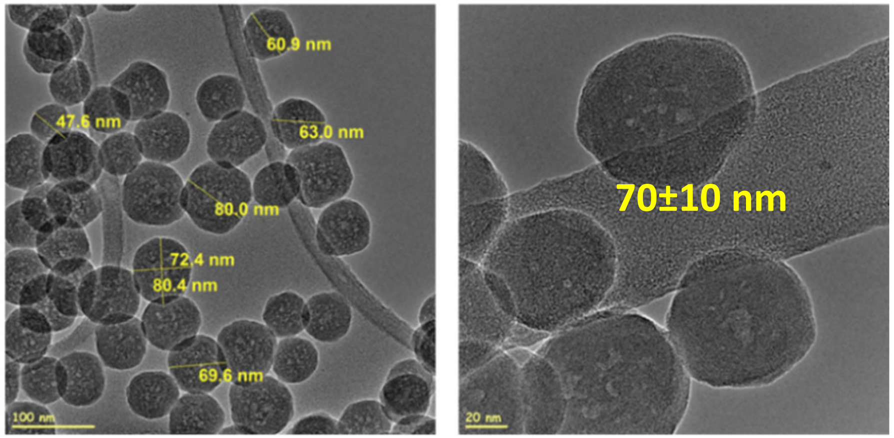
1. Synthesis of permanent cavitation resistance, non-leaching anti-fouling coatings

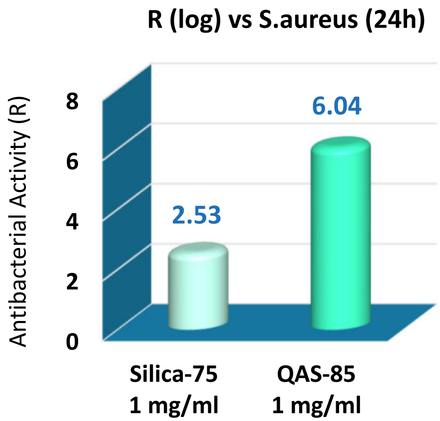
Synthesis of **biocide functionalised silica nanoparticles**



Transmmision Electron Microscopy (TEM):



Antibacterial activity of nanoparticles against Staphylococcus aureus bacteria:



Nanoparticles	DLS (nm)	TEM (nm)
NP-85	85	70±10

Functionalized nanoparticles presented high antibacterial activity.

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2. Development of highly crosslinked PUD for cavitation and antifouling resistance

Synthesis of biocidal **elastomeric polyurethanes** by two strategies:

Strategy 1

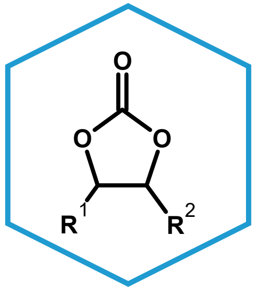
Fluorinated building blocks

Decreasing the surface energy

Solvent based 2 component fluorinated polyurethanes

Strategy 2

H-NIPUs

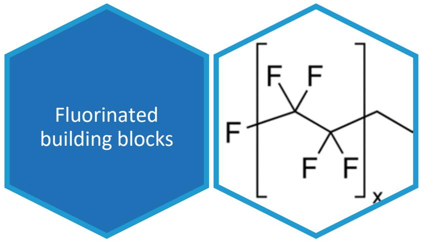


Insertion of cationic groups

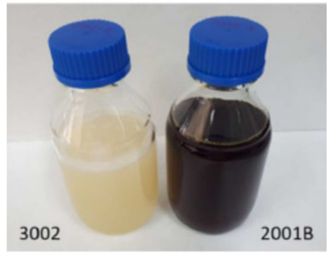
Water based 1 component cationic polyurethanes

2. Development of highly crosslinked PUD for cavitation and antifouling resistance

Strategy 1



		Component A FUNDITEC	Component B commercial
Solvent based 2K fluorinated polyurethanes (FPU)	**Type I**	Fluorinated polyisocyanate	Acrylic polyol
	Type II	Acrylated polyisocyanate	Fluorinated polyol



Acrylated (left) and fluorinated (right) polyisocyanates synthesised by FUNDITEC

Physical properties of 2K FPU coatings applied on CANOE composite substrates:

Code	Hardness	Adhesion	Tg (°C)
Type I	H	5B	23,8
Type II	4H	5B	28,8

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2. Development of highly crosslinked PUD for cavitation and antifouling resistance

Strategy 2

Ammonium quaternary salts

	Component A FUNDITEC	Component B commercial
Water based 1K cationic polyurethanes (PUD)	Polyurethane aqueous dispersion	-

Water-based polyurethane dispersion PUD5 synthesised by FUNDITEC

Physical properties of 1K PUD coatings applied on CANOE composite substrates:

Code	Hardness	Adhesion	Tg (°C)
Coating PUD	5H	5B	44,6

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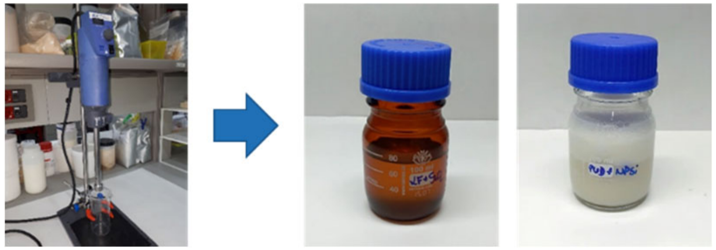
3. Incorporation of silica nanoparticles into the polyurethane matrix

<u>Step 1</u>: Dispersion of silica NPs (1%wt) in PUD matrix in:

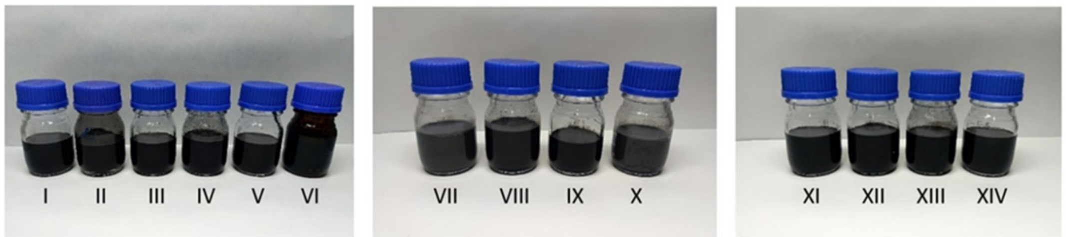
- Bicomponent fluorinated polyurethanes coatings, or in
- Single component water-based PUD



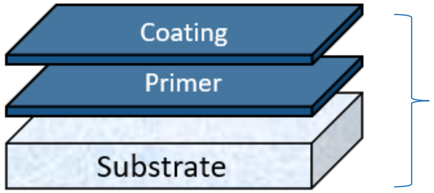
<u>Step 2</u>: Incorporation of carbon nano-complexes for improving cavitation resistance:

Dispersions were prepared by mixing:

- ➢ A novel mix of **carbon nano-complexes** developed by SPNano containing SP1 protein and different nanoparticles (NP) such as: MWCNT, SWCNT, graphene and CB,
- ➢ **Dispersions of silica NP** obtained in step 1 (NP + 2K or 1K coatings)



4. Application of coatings on composite substrate



1x 100µm PU coating

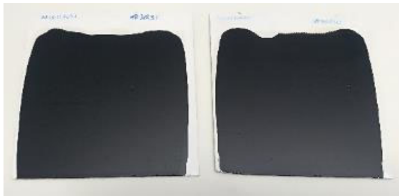
1x 120µm Hempel Primer 45550

Substrate: composite with gel coat (CANOE)

Code	Formulation
Primer	Commercial primer
7688W	Commercial topcoat
76890	Commercial topcoat

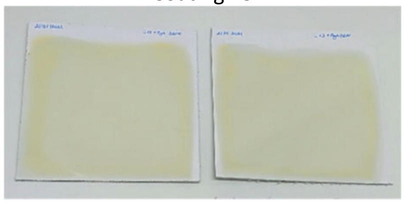
7688W

76890



Code	Formulation
Coating 13	2 components: 2001B + Uralac T cat. XK-651 Additives

Coating 13



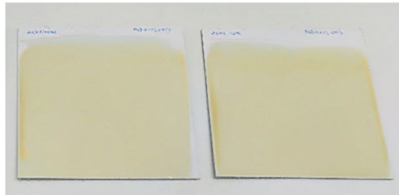
4. Application of coatings on composite substrate

Code	Formulation
Coating 15	2 components: 3002 + LF910 T cat. XK-651 UV cat. Irgacure 184 Additives
Coating 15 + CNP10	+ 0.1% CNP10
Coating 15 + SiO_2	+ 1% SiO_2

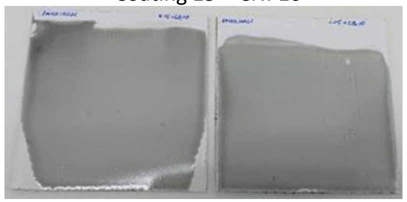
Code	Formulation
PUD5	1 component: PUD5 UV cat. Irgacure 2959 Additives
PUD5 + CNP5	+ 0.1% CNP5
PUD5 + SiO_2	+ 1% SiO_2

Coating 15

PUD5

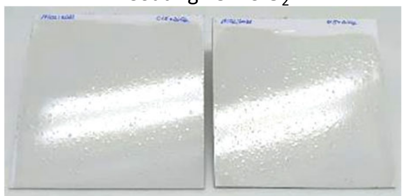


Coating 15 + CNP10

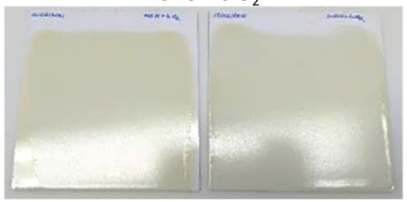


PUD5 + CNP5

Coating 15 + SiO_2



PUD5 + SiO_2



5. Testing of coatings

Biofouling and cavitation resistance:

- Two **fouling field tests**:
  - ✓ HarshLab in the Bay of Biscay (Spain)
  - ✓ Dynamic antifouling test rig in Dublin (Ireland)
- Cavitation tests in the lab

Tecnalia's Harshlab facility
Bay of Biscay (Spain)

DCU's dynamic antifouling test rig
Dublin (Ireland)

FUNDITEC's Set-up of cavitation erosion test

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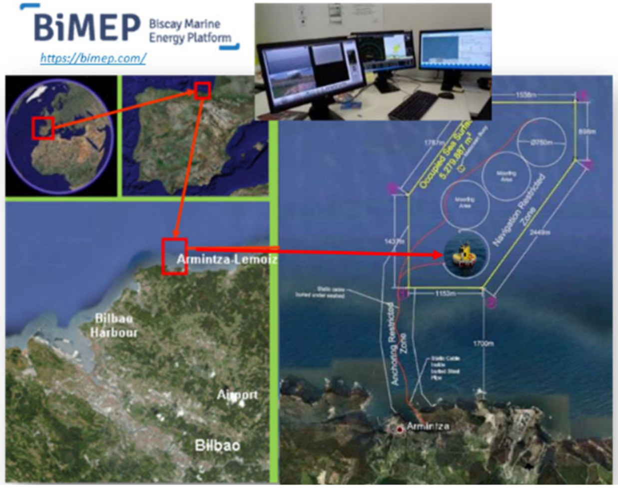
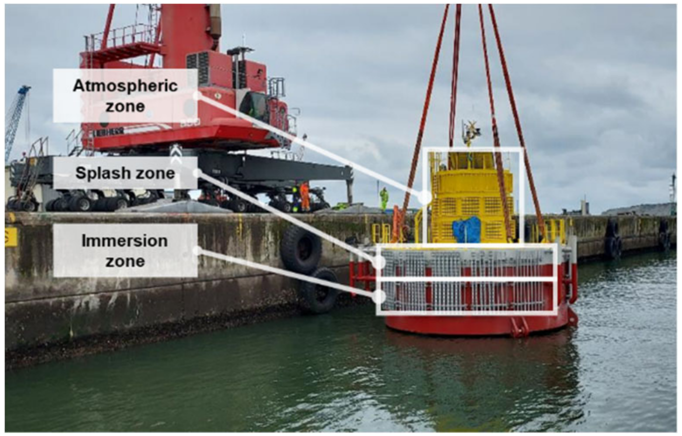
5. Testing of coatings

HarshLab
OFFSHORE MATERIALS & COMPONENTS LAB

https://harshlab.eu/en/

BiMEP Biscay Marine Energy Platform
https://bimep.com/





TECHNICAL SHEET

Dimensions: 8,5 m diameter; 7,0 m high, 120tons

Capacity

- Exposition of more than **2000 samples** in atmospheric, splash and immersion zones
- Space for component testing: **120 m²** (60 m² outdoor deck, 57 m² in hold)
- Main crane capacity: **1 ton** @ 5,25 m
- Auxiliar davit capacity: **300 kg** @ 1,5 m
- Maximum payload: **9 ton**.

Grid connected (spring 2023)

- Umbilical cable for **power and communications**
- Connected to BiMEP's submarine grid at 690V/160 kVA
- Internal working voltage: alternating current at 400V and 230V, and direct current at 24V and 12V
- Local photovoltaic and batteries system for feeding essential equipment onboard (AIS, lantern, etc)
- Designed for connecting third party devices testing in BiMEP area to the submarine grid.

Tecnalia's Pasaia Port

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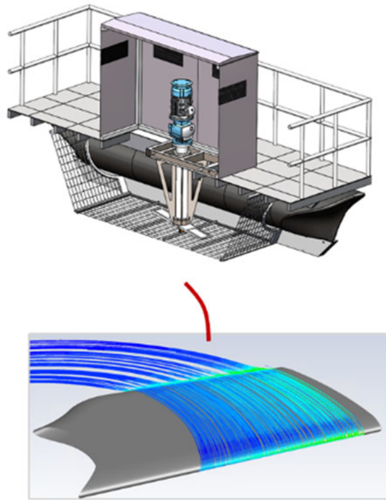
5. Testing of coatings

Dynamic antifouling test rig (Dublin)

Designed and built to study **antifouling** properties under **dynamic conditions in an estuarine environment**

Key Characteristics

- Two blade impeller with symmetrical flat profile
- Impeller **diameter**: **1.2m**
- Max Rotational speed: **286 RPM**
- **Uniform** stress distribution for given radial position
- **Hydrodynamic stresses** increasing radially to $\sim 500\ N/m^2$



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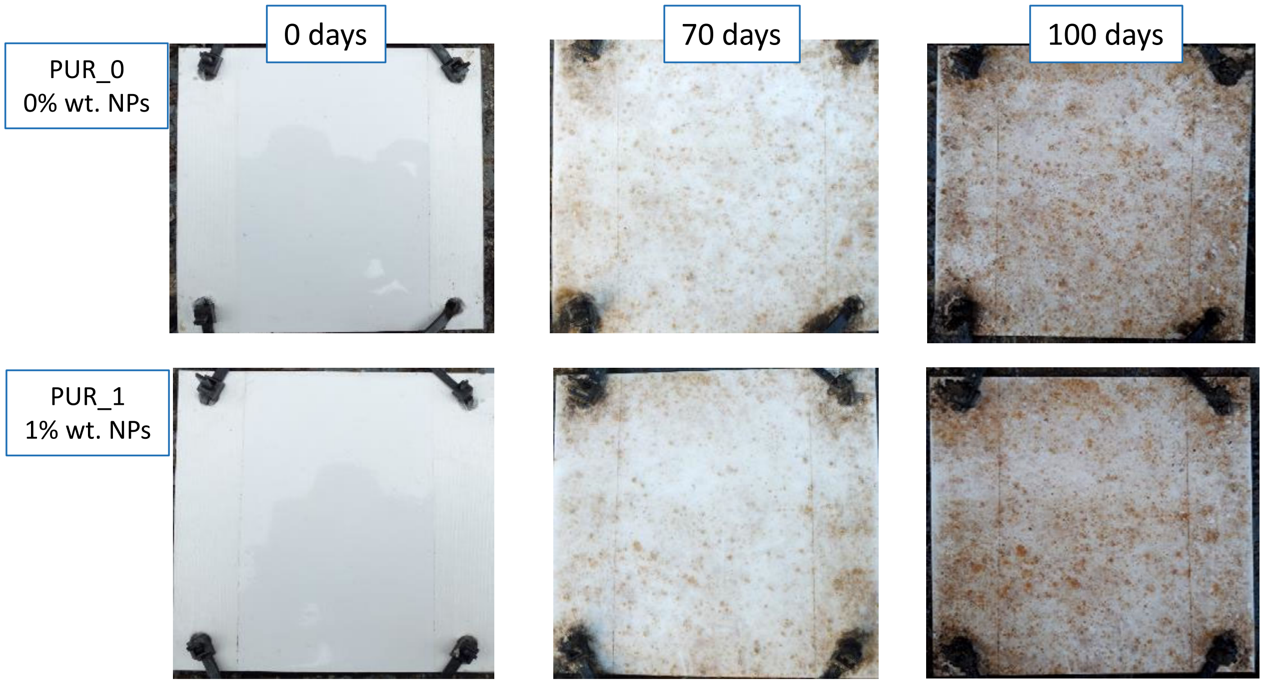
6. Preliminary results

Influence on NPs on biofouling resistance by exposure on static sea immersion conditions in the Bay of Biscay

Composites + gelcoat + PUR with NPs (100 °C/1h)

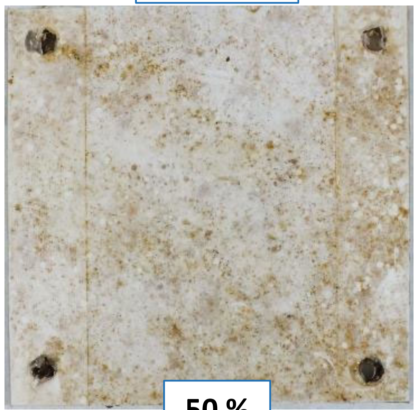


6. Preliminary results

Influence on NPs on biofouling resistance by exposure on static sea immersion conditions in the Bay of Biscay

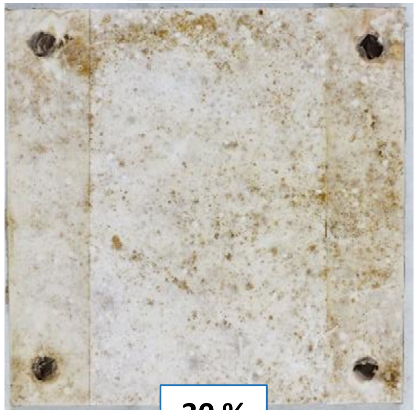
Ref.	Substrate	NP-85 (% wt.)	% Fouling
PUR_0	Composite + Gelcoat	0	50 %
PUR_1	Composite + Gelcoat	1	30 %

PUR_0
0% wt. NPs



50 %

PUR_1
1% wt. NPs



30 %

*The percentage cover of fouling was **reduced 20 %** compared to control system without nanoparticles*

Fouling coverage measured according ASTM D6990-05 “Standard Practice for Evaluating Biofouling Resistance and Physical Performance of Marine Coating Systems”.

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6. Preliminary results

Lab cavitation erosion tests

Code	0 min	1 min	2 min	3 min	4 min	5 min	% mass loss	Adhesion	Hardness
Commercial 7688W (white)							2,0286	0B	B
Commercial 76890 (black)							2,5881	0B	B
Coating 13							0,6385	5B	H
Coating 15							0,0187	5B	4H
Coating 15 CNP							0,0350	5B	4H
Coating 15 SiO_2							0,0813	5B	4H
PUD							0,0175	5B	5H
PUD CNP							0,1576	5B	5H
PUD SiO_2							0,0415	5B	5H

- ✓ Improved **erosion resistance**,
- ✓ Better **adhesion** and **hardness** compared to commercial ones.
- ✓ Incorporation of carbon and silica NP has **no effect** on erosion resistance, adhesion or hardness values.
- ✓ **Best topcoats** (so far): Coating 15 and PUD.

6. Preliminary results

Stay tuned for further results!!

http://nemmo.eu/

Coatings and composites are **currently being evaluated** for:

- Further data on **ageing resistance** (accelerated and field testing)
- Antifouling behaviour under **dynamic conditions**
- **Fatigue and impact** resistance
- Further data on **cavitation wear testing**

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Thanks for your attention!

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