

IZADI-NANO2INDUSTRY

*“Compounding of polymer materials
and nanotexturing of the mould -
sector: Automotive”*

**PhD. Cristina Elizetxea, TECNALIA
Project Coordinator**

GA 686165

NN18, Thessaloniki, Greece
July, 05 – 2018

IZADI-NANO2INDUSTRY

Project Overview



Consortium



Technical University of Denmark



Call

H2020-NMP-PILOTS-2015



Topic

NMP-02-2015-Integration of novel nano materials into existing production lines



Funding scheme

IA – Innovation action



EU contribution
EUR 6.027.653



Coordinated in
Basque Region (Spain)



In **IZADI-NANO2INDUSTRY** Injection moulding, Casting and Coating manufacturing processes will be improved by nanotechnology to enable industrial scale production of new performance-enhanced components



- **IZADI-NANO2INDUSTRY** aims at contributing to overcome the barriers that nano-materials are currently facing to get introduced in the market based on “**Safe by Design**” Strategy.
- Technologies based on **nano-reinforced materials**, **nanotextured surfaces** and **nanostructured-coatings** have been implemented in three innovative PILOTS:
 - ✓ **TRIBONANO**: Thermal Spray Technology for Nanostructured Coatings by Solid State Deposition
 - ✓ **HARDCAST**: New Gravity Casting Process for Nano-Reinforced Metal Parts
 - ✓ **ESTCRATCH**: Innovative Injection Moulding Process for Nano-Reinforced and Nanotextured Plastic Surfaces
- Proposing new **added-value products** to OEMs and solutions to the European Automotive, Construction and Agricultural Machinery sectors.

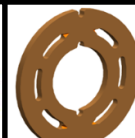
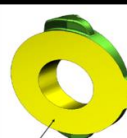
Technology	Requirements	Sector	IZADI-NANO2INDUSTRY		
			Components	Pilot (TRL7)	Company/Place
Nano-reinforced thermoplastic (based on master-batches)+ Nanotextured surfaces	Anti-scratch and aesthetic properties	Automotive	B-pillar	ESTCRATCH (Injection moulding)	MAIER/Basque Region
Nano-reinforced metal castings (based on master-ingots)	Hardness, resistance temperature	Construction Agricultural machinery	Swash plate	HARDcast (Gravity casting)	FMG/Lombardy Region
Nano-structured coatings (based on nanostructured powders)	Wear	Construction Agricultural machinery	Valve plate	TRIBOnano (Coating by solid state deposition)	TECNALIA Basque Region



**B-PILLAR
ESTCRATCH**



**SWASH PLATE
HARDcast**



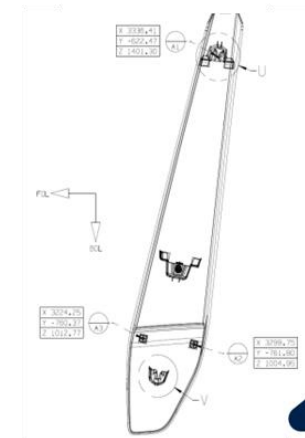
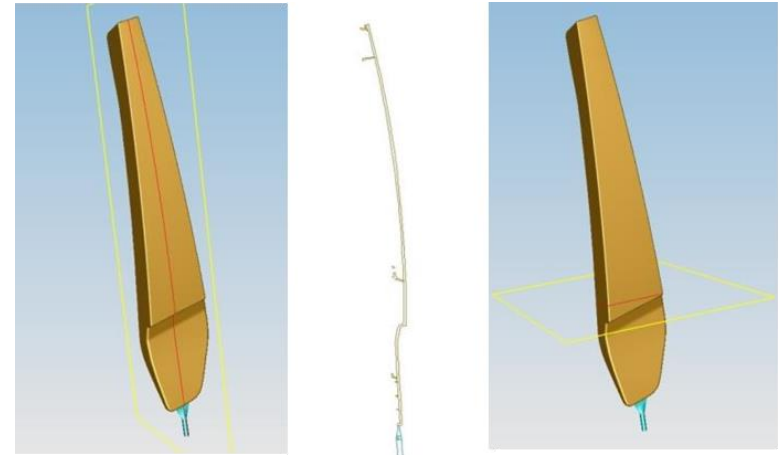
**VALVE PLATE
TRIBOnano**

IZADI-NANO2INDUSTRY, ESTCRATCH PILOT:

“Compounding of polymer materials and nanotexturing of the mold-sector: Automotive”

Part Specifications according to MAIER request:

- Initial design: Based on the B-Pillar from Opel Meriva 2010
- General dimensions: 650 x 100 mm
- Thickness: 3.5 mm
- Weight: 280 g (PMMA)
- Part fixed to the car body with three clips



Part Specifications according to MAIER request:

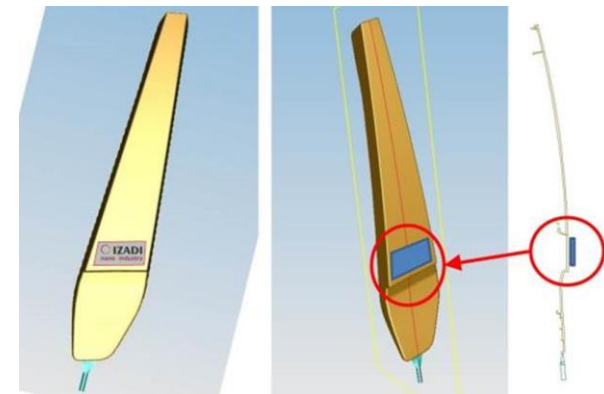


Scratch resistance improvement

- Development of PMMA compounds with better resistance to scratch than commercial grades in the market.
- Addition of specific nanofillers by extrusion compounding.
- Amount and kind of nano-additives to be defined (lab and pre-industrial scale)

Plasmonic aesthetics

- Development and evaluation of new aesthetical finishes on automotive plastic parts, based on plasmonic fields on the visible surface of the injected parts.
- Design of B-Pillar injected on PMMA with a field colored by plasmonic effect.
- Injection mold with nanotextured inserts on the surface of the cavity.
- Injected B-Pillar sample parts with Aesthetic Finish:
 - High gloss
 - In-Mass colored (Piano Black)
 - Plasmonic Pattern (e.g. IZADI-NANO2INDUSTRY logo)



Scratch Resistance Improvement Strategies



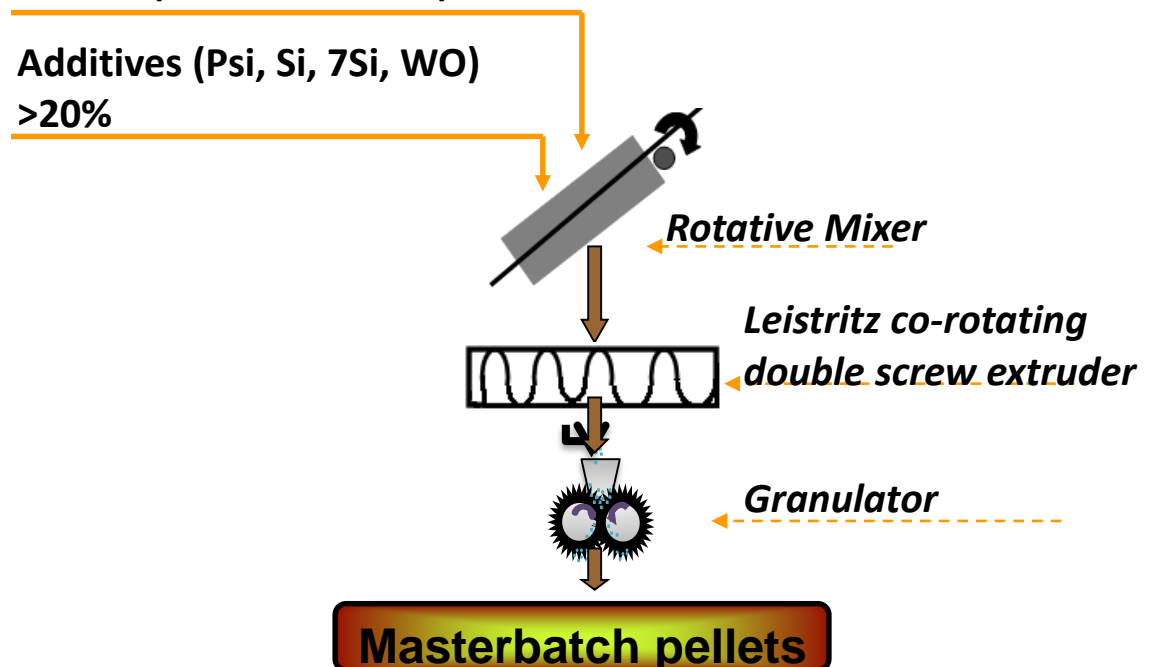
Material Selection:

- Thermoplastic Matrix: PMMA
- Additives: Psi
Si
7Si
WO

Masterbatch Preparation (1):

PMMA (Nature or Black)

Additives (Psi, Si, 7Si, WO)
>20%





Masterbatch Dilution (1):

Masterbatches prepared by ICECHIM:

- 20% Psi:
- 20% Si:
- 20% 7Si:
- 20% WO:

20Psi

20Si

207Si

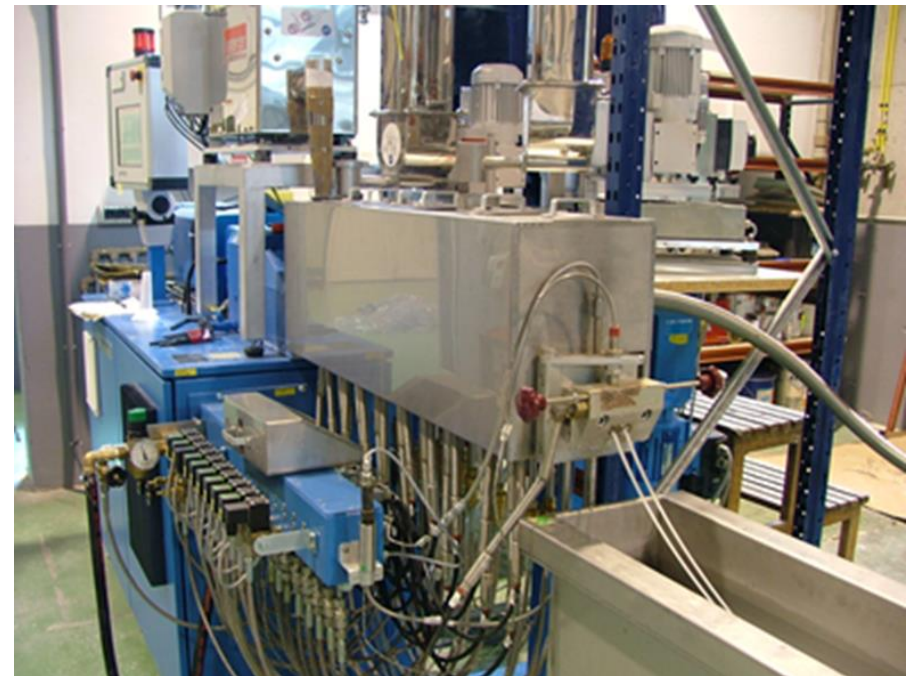
20WO



Diluted to a final content of 2% nanofiller with PMMA to prepare 7 different formulation

Formulations prepared by TECNALIA:

- PMMA 2 Psi
- PMMA 2 Psi + 2 Si
- PMMA 2 Si
- PMMA 2 Psi + 2 7Si
- PMMA 2 7Si
- PMMA 2 Psi + 2 WO
- PMMA 2 WO

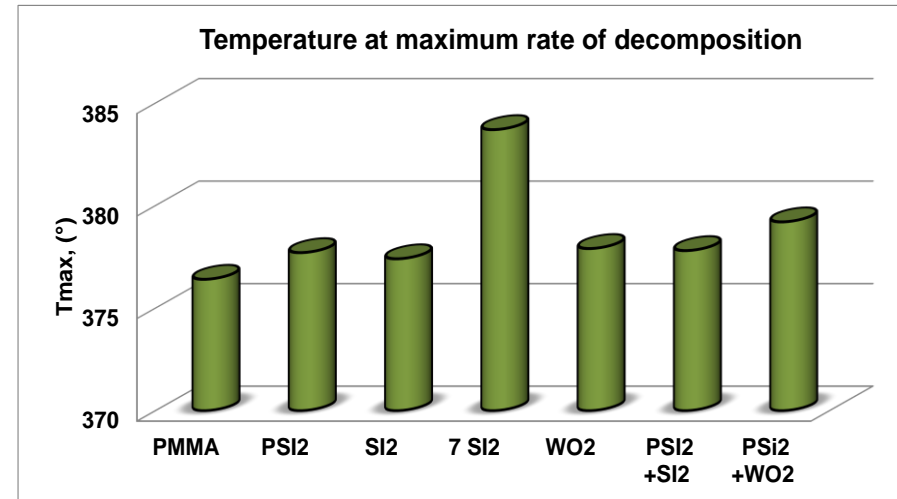
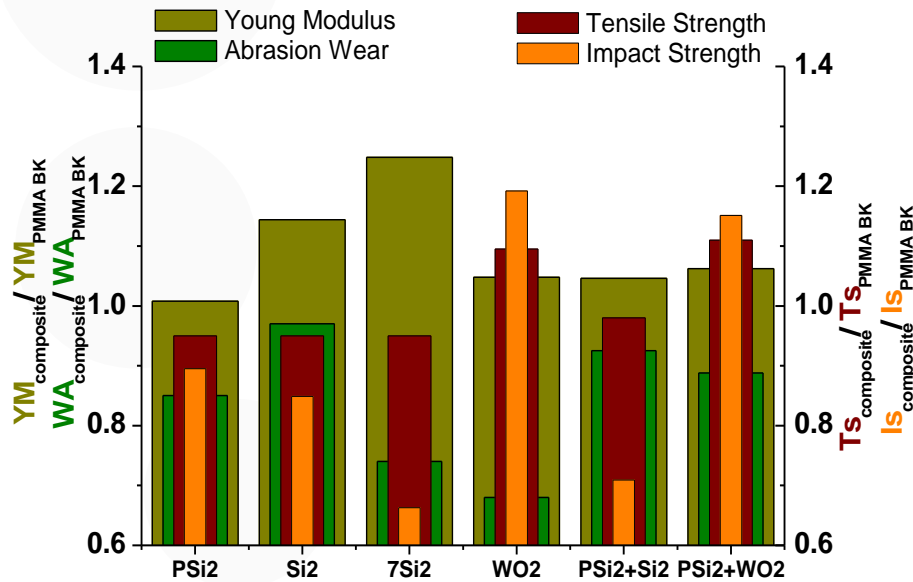


COPERION ZSK 26 MEGA COMPOUNDER Twin-screw extruder

Formulation Characterization (1):



The effect of (nano)reinforcing agents on mechanical and thermal properties of composites based on PMMA



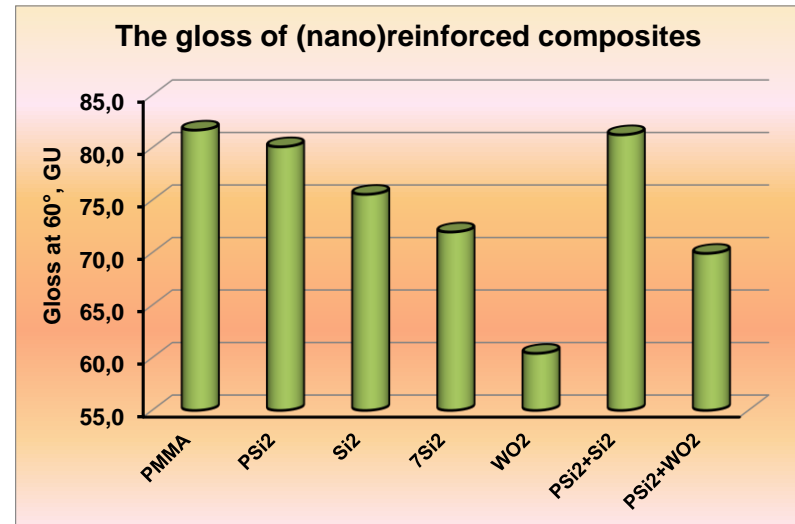
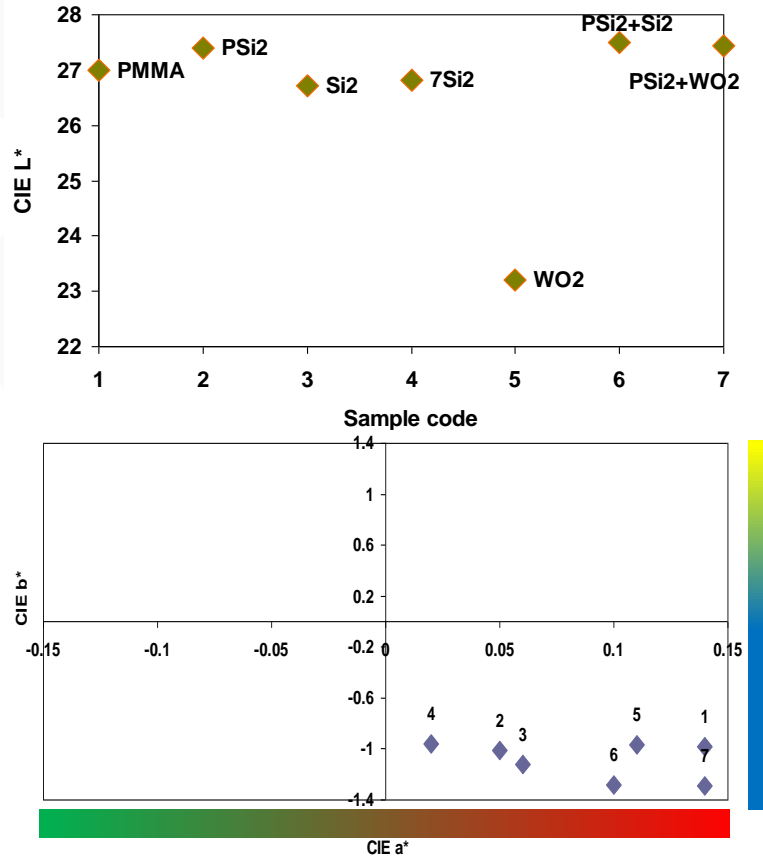
- With WO the best mechanical properties;
- With PSi2+WO2 very promising results

- With 7Si2 the best thermal stability;
- With PSi2+WO2 very promising results

Masterbatch Characterization (1):



The effect of (nano)reinforcing agents on aesthetic properties of composites based on PMMA



- With **PSi2+Si2** the best aesthetic properties
- With **PSi2+WO2** very promising results



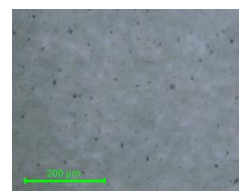
Masterbatch Preparation (2):

- **PMMA-(W0+PSi) nanocomposite** improves significantly all the mechanical properties of PMMA BK, but decreases the gloss. Promising results but not for aesthetical application. **Further trials will be performed trying to improve aesthetical performance.**
- **PMMA-(Si+PSi) nanocomposite** exhibits significantly enhanced scratch resistance, lower abrasion wear and lower variation of gloss by dry abrasion in comparison with PMMA BK. **These excellent properties make it suitable for B-pillar injection moulded.**
- Using ICECHIM facilities **6 new masterbatches** were obtained: **mbPSiSi20, mbPSiSi30, mbPSiSi40, mbPSiWO20, mbPSiWO30, and mbPSiWO40.**

Properties	mbPSiSi20	mbPSiSi30	mbPSiSi40	mbPSiWO20	mbPSiWO30	mbPSiWO40
Density, g/cm ³	1.1965±0.005	1.2067±0.0009	1.2251±0.0002	1.2076±0.0006	1.2108±0.0004	1.2151±0.003
MFI, g/10 min	8.35±0.99	11.23±0.08	19.13±0.83	48.2±1.98	54.6±0.2	110.16±1.66
Weight loss at 240°C, %	0.24±0.06	0.20±0.05	0.26±0.07	0.37±0.01	0.34±0.01	0.28±0.02

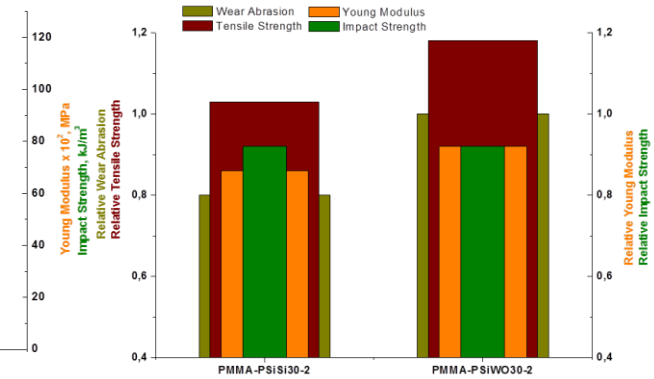
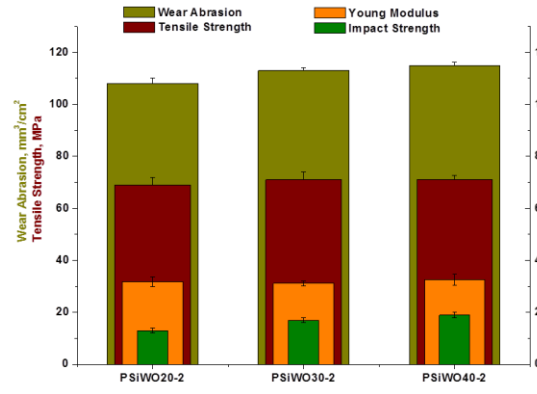
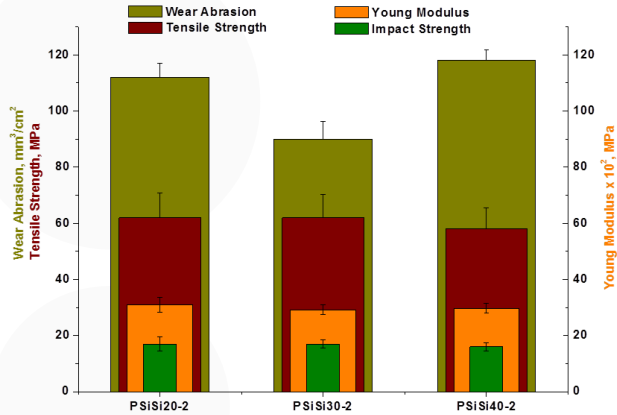


mbPSiSi granules

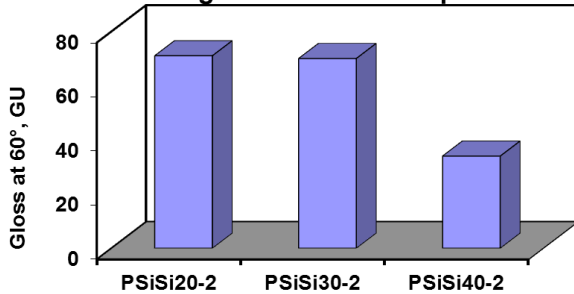


Optical microscope photo of mbPSiSi

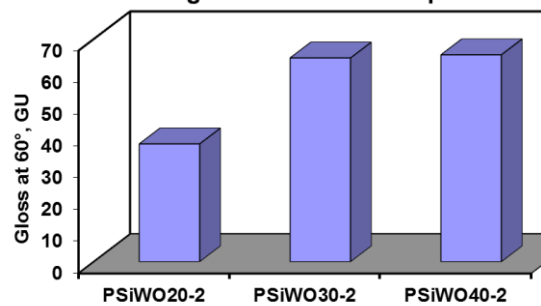
Masterbatch Dilution and Material Characterization (2):



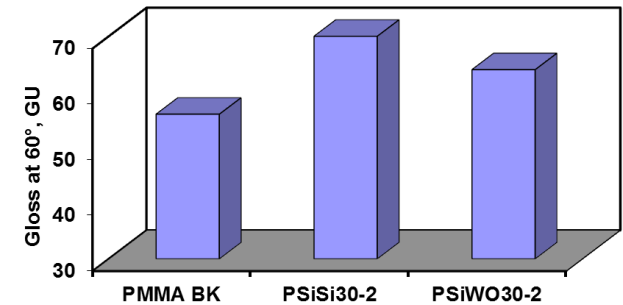
The gloss of PSiSi composites



The gloss of PSiWO composites



The gloss of PSiSi/WO composites vs. PMMA



The best properties were obtained for nanocomposite based on **2%PSi** and **2%Si**. By dilution of **mbPSiSi30** more homogenous nanocomposite (**PMMA-PSiSi**) with improved properties was obtained.

PMMA-PSiSi formulation selected for B Pillar manufacturing

New aesthetical finishes on automotive plastic parts

- Design and development of specific **design** of plasmonic color metasurface decoration
- Development of the **steel patterning** technology to fabricate a well-defined nanostructure in the tool surface
- Delivery of an **injection moulding** tool insert for injection moulding validation



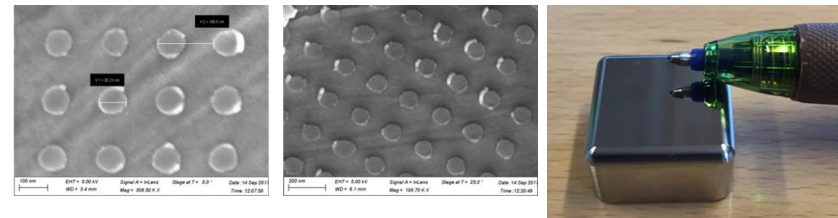
B-pillar insert with diffractive colors



Diffractive colors (angle dependent)

- Large nanostructures – easier to imprint, etch and mould
- Low tolerance
- Close to market
- Does not require metal layer – only plastic

20x20 insert with plasmonic colors

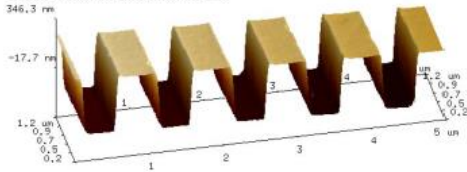


Plasmonic (angle independent)

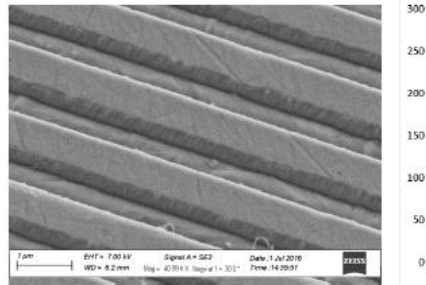
- Color palette
- Can be protected with durable coating
- Very little commercial competition

Diffractive insert into Flat Plates:

Diffractive gratings on steel insert



Inserts by TOOL
Nanoimprint by NILT
Etching by CSA



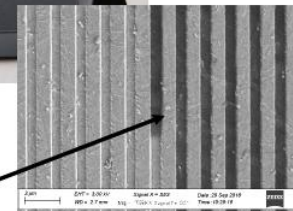
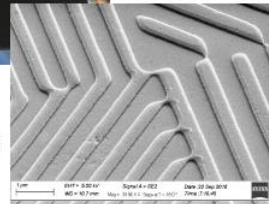
Technical University of Denmark



MICHAELLUNDBECH
INTELLIGENT TOOLING



Well-defined
pattern on
PMMA part



PMMA
residues on
insert surface

Diffraction insert into B-Pillar Injection Tool:





Nano reinforced B-Pillar Diffractive Parts :





Validation Tests on Nano-Reinforced B-Pillar Diffractive Parts :

		Material Code	IZ044	IZ019	IZ033	IZ043
		Type	ABS	ASA	PMMA	PMMA-(PSi+Si)4
Validation Test	Method	Specification				
Weight (LH)	(g/part)		282,3	291,2	336,3	334,6
	(%)		100	103	119	119
Chemical Resistance	D27 5437	≥ 3 min				
	Ethyl Alcohol / 3 min		OK	OK	OK	OK
	Ethyl Alcohol / 10 min		OK	OK	OK	OK
	Xylene / 3 min		Not Good	Not Good	OK	OK
	Xylene / 10 min		Not Good	Not Good	OK	Not Good
Colour (Light Cabin)	ISO 3664					
Colour Fastness to Rubbing (Crockmeter)	D45 1010 /ISO 105 F09	50 Cycles Degradation ≥ 4				
	50 Cycles		?	OK	OK	OK
				4/5	5	5
	100 Cycles		?	OK	OK	OK
				4/5	5	5
	200 Cycles	Not Good	Not Good	Not Good	Not Good	
			4	4/5	4/5	
Resistance to immersion in water (Ford Tank)	D27 1327	40°C/ 240 h Colour variation = 0				
	40°C/ 4 days		OK	OK	OK	OK
	40°C/ 7 days		OK	OK	OK	OK
	40°C/ 10 days		OK	OK	OK	OK
Stone Impact Resistance (Erichsen 500SAE)	D24 1312	<2		OK	OK	OK
Heat Resistance (1h/90°C)						
Impact Resistance (500g/50cm/23°C)						
Aesthetic			OK	OK	OK	OK

Health, safety and environmental issues in IZADI-NANO2INDUSTRY, ESTCRATCH PILOT



The project IZADI-NANO2INDUSTRY aims to implement the “master-batches, master-pellets and the nanostructured powders in three innovative PILOTS (ESTCRATCH, HARDcast and TRIBOnano) integrating **safe-by-design approaches** into the developments stages. The project follows to develop inherently **safer production methods**.

General framework

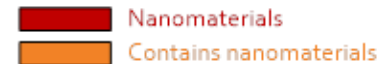
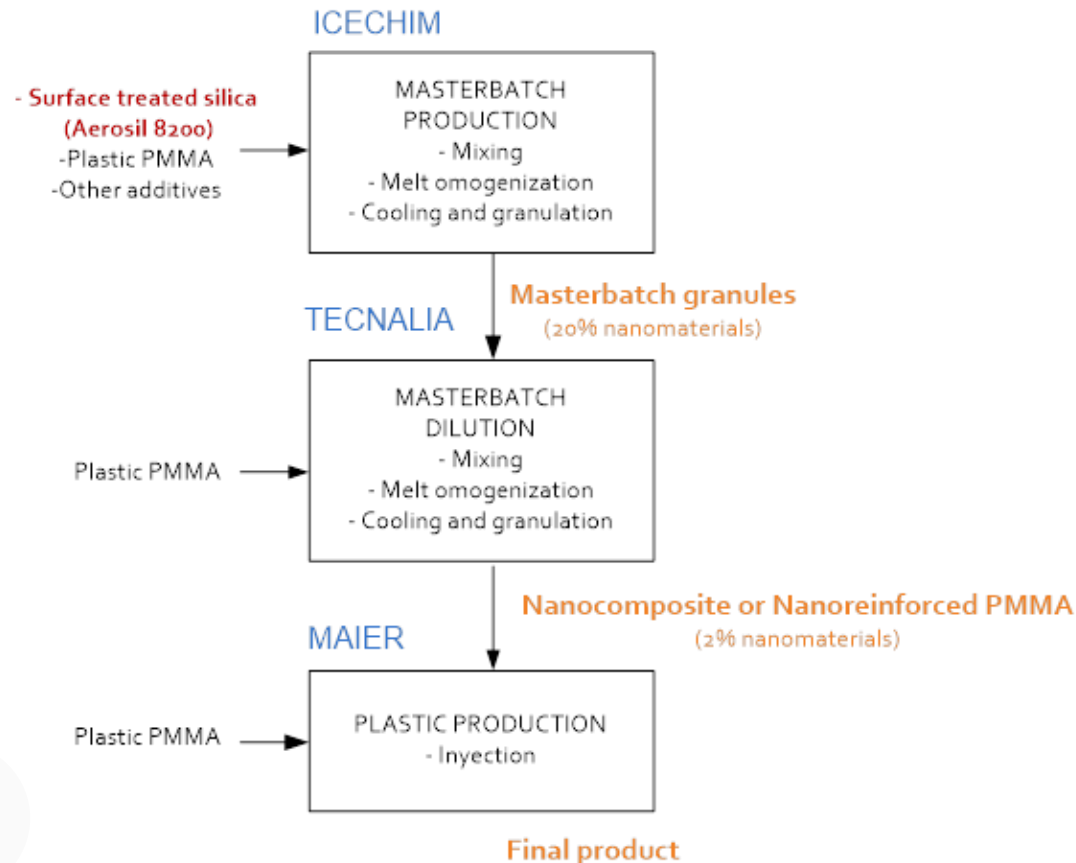
1. Information gathering

- Product information (Safety Data Sheet, Bibliography, SEM images...)
- Exposure information (Visits factories such as Icechim, Tecnalia and Maier)

2. Risk assessment according to the Technical Specification ISO/TS 12901-2

“Nanotechnologies-Occupational risk management applied to engineered nanomaterials, part 2: use of the control banding approach

Health, safety and environmental issues , ESTCRATCH PILOT





1. Information gathering

Product information

- **Synthetic amorphous silica (Nanomaterial)** : Aerosil R8200 (Silanamine, 1,1,1-trimethyl-N-(trimethylsilyl)-, hydrolysis products with silica)
 - Information
 - ✓ Powder
 - ✓ Main primary particle size: 5-50 nm (spherical)
 - Toxicity
 - ✓ Bibliography: posible lung effects but mostly reversible after the cessatin of exposure.
 - ✓ Safety Data Sheet: no toxicological test are available on the product, no ecotoxicological data is available for this product
 - ✓ Explosiveness: not flammable solid
- **Final product (nanocomposite)**
 - 2% of Aerosil R8200 strongly bound to a plastic

Exposure scenario at industrial production lines

- Cooling and removal of the plastic piece from the metal mold (the mixed material containing nanomaterial is exposed to high temperature, meaning potential thermal degradation and emission of otherwise entrapped particles).
- Cleaning and maintenance (Cleaning of metallic mold with Isopropyl alcohol, change of mold)
- But Only 2% of Aerosil R8200 is embedded in a matrix (98% of PMMA). Further, in Maier the injection is done with 95%of PMMA-BK and 5% of nanocomposite, so the likelihood for the nanoparticles to release free in the workplace is low.



2. Risk assessment at industrial production lines (Plastic injection)

- **Health**

Even though exposure is low, such as there is no conclusive data indicating that the nanomaterial is not toxic, it's recommended to place a local ventilation (precaution principle)

- **Security**

Masterbatches (granules) no ATEX risk

- **Environment**

The following waste is generated:

- Contaminated wipes
- Pieces which contains nanomaterials (solid matrice with nanomaterials that are not friable)

They must be managed with an authorized manager



Project Coordinator

Cristina Elizetxea Ezeiza
cristina.elizetxea@tecnalia.com



Project Scientific Coordinator

Maider Garcia De Cortazar
maider.garciadecortazar@tecnalia.com



<http://www.izadinano2industry.eu>