CONTROL OF MATERIAL RELEASE DURING THE OUTDOOR USE OF POLYMERIC NANOCOMPOSITES CONTAINING TIO_2 NANOPARTICLES

07-10th November 2016
Minatec-Grenoble, France

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Project funded from the European Union's Seventh Framework Programme (FP7/2007-2013)
under grant agreement nº604387.

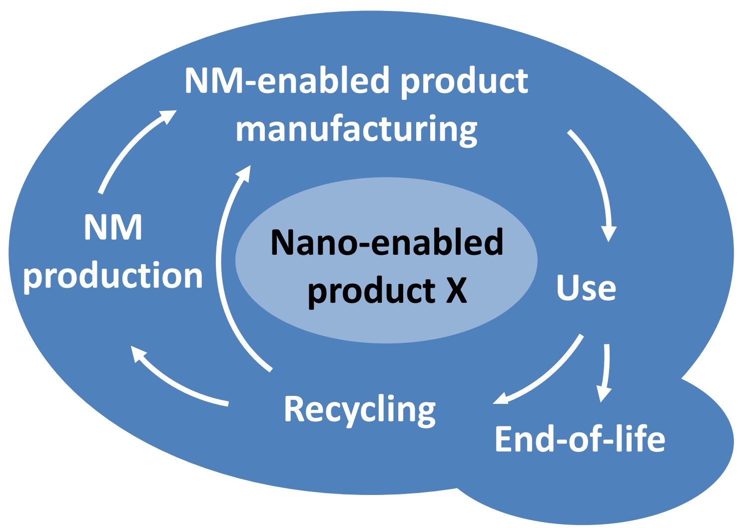
General objective

OBJECTIVE

Develop innovative methodologies to **evaluate** and **manage** human and environmental health risks of NM-enabled products, considering the whole product life cycle

GUIDEnano Tool

NM-enabled product Life Cycle

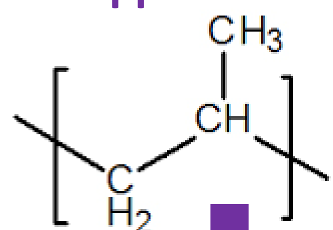


WP3 Objective

The wp3 main objective is to identify and predict release of NM throughout the life cycle of NM-enabled products; a strategy that will be implemented in the **GUIDEnano Tool**

Case study: PP nanocomposites for automotive applications

PP



PP
PP + UV stabilizer
PP + 3% TiO_2
PP + 1% TiO_2 + UV stb.
PP + 3% TiO_2 + UV stb.
PP + 5% TiO_2 + UV stb.
PP + 3% TiO_2 (C.G.) + UV stb.

PP + 3% TiO_2@SiO_2
PP + 3% TiO_2@SiO_2 + UV

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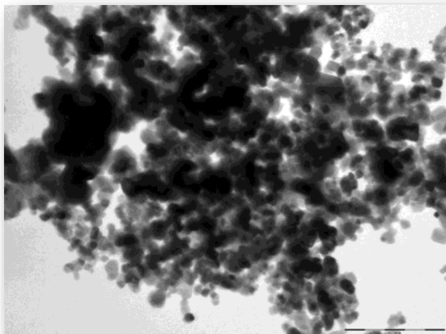
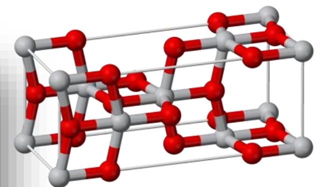
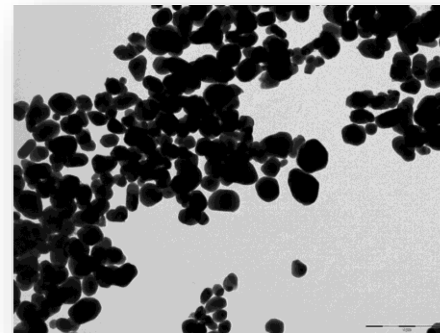
Sample Characterization: TEM/XRD/RAMAN Analysis

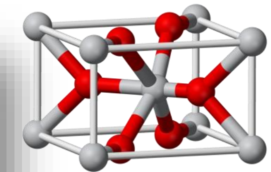
TiO_2 NP Anatase *vs* TiO_2 NP Rutile



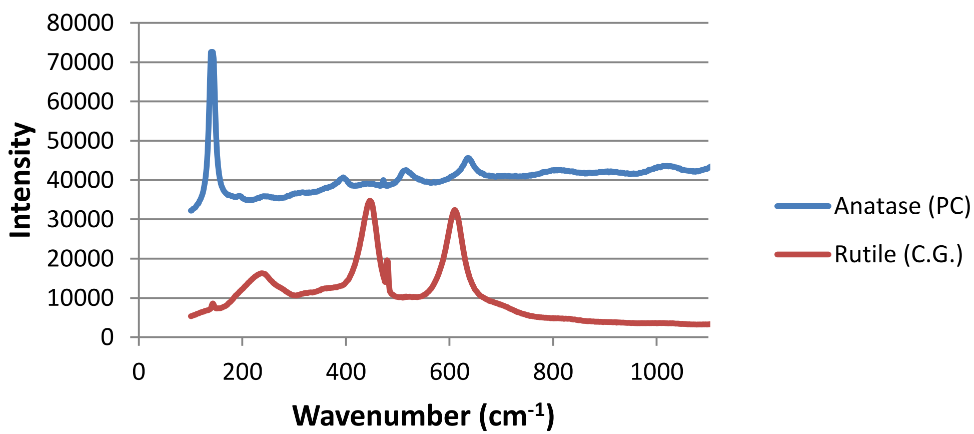


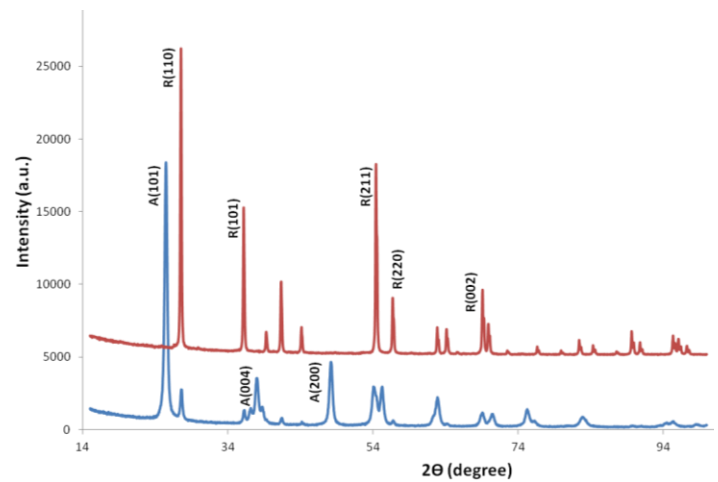
20± 4 nm (TEM)
Anatase (tetragonal dipyramidal)





200± 40 nm (TEM)
Rutile (tetragonal)





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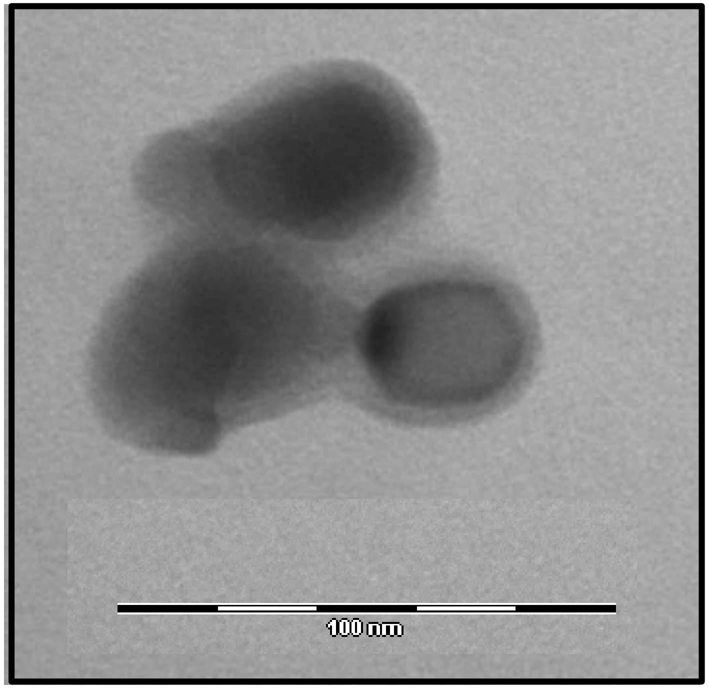
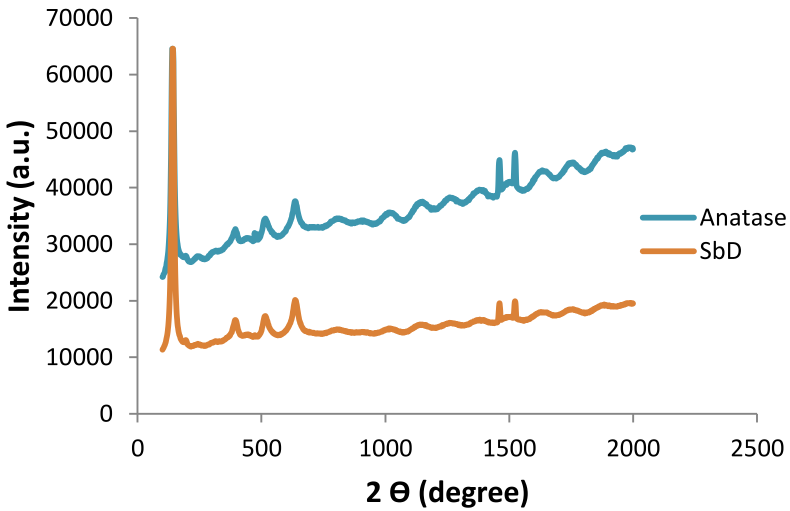
Sample Characterization: TEM Analysis

Safer-by-design Particles: TiO_2 NPs coated with SiO_2



(TiO_2@SiO_2, 25 nm@3 nm)



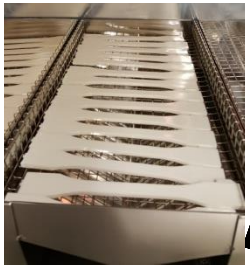
SbD dogbone
PP + 3% TiO_2@SiO_2
PP + 3% TiO_2@SiO_2 + UV_{st}

Outdoor Simulation ageing

Experimental

PP samples were aged in a climatic chamber following standardized protocols (modified ISO 4892-02:2006 conditions), samples aged at different times (500, 750,1000 h)

Runoff waters were collected every 200 h and freeze-dried to analyze the released material



Dogbone analysis // Runoff water analysis

SEM // TEM

Weight change

IR

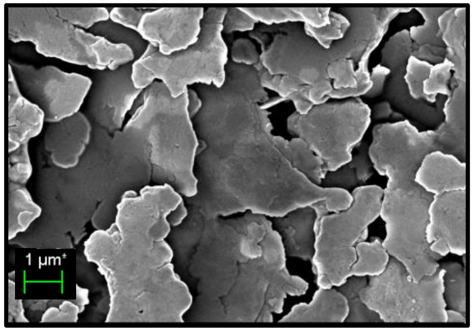
Thermal properties

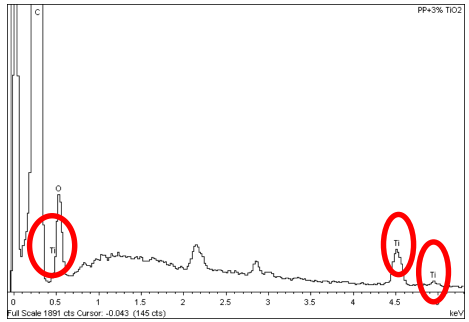
Mechanical properties

Irradiation (340 nm)	0.50 W/m^2
Internal filter	borosilicate
External filter	borosilicate
BST temperature	65ºC (±3ºC)
Relative humidity	50% (±5%)
Wetting cycle	1 ± 0.5 min
Drying cycle	29 min
Irradiation	Continuous
Total exposure	1000 h

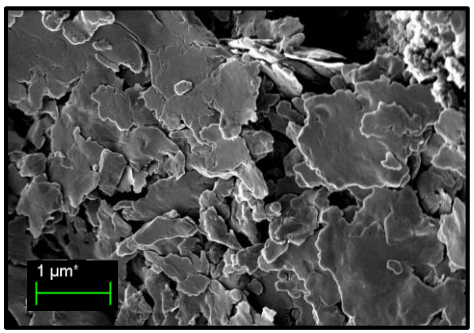
Sample Characterization: SEM/ TEM Analysis

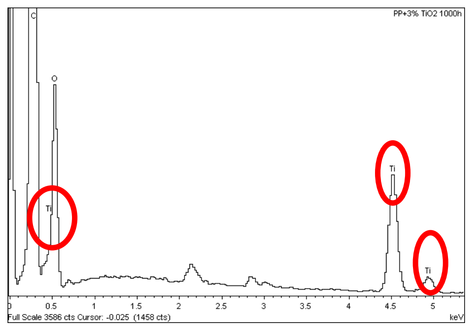
PP + 3 % TiO_2





Aged PP + 3 % TiO_2

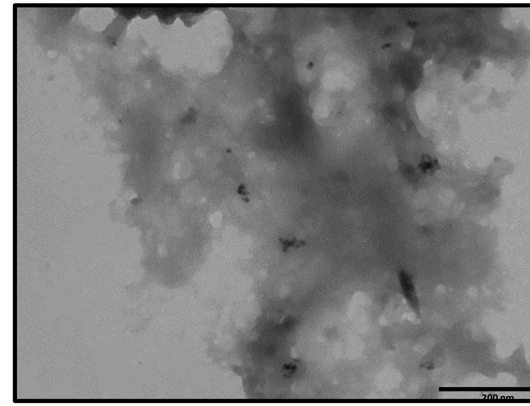


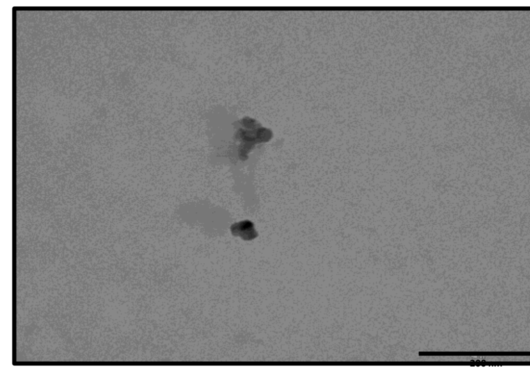


Polymer surface degradation could be observed after ageing

TiO_2 NP migration to the polymer surface was confirmed by EDX

Runoff waters from ageing
PP + 3 % TiO_2

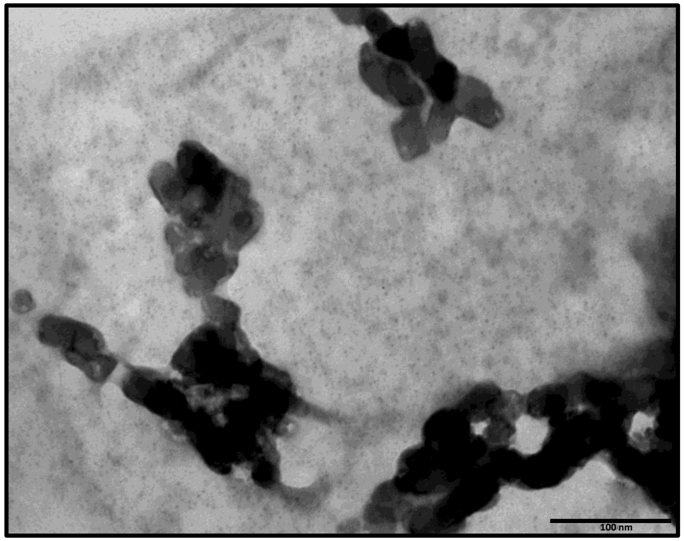




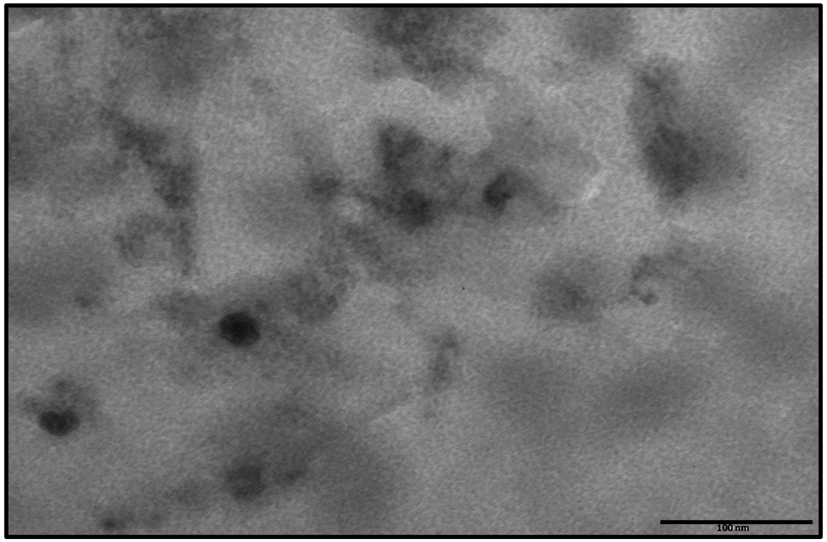
TiO_2 NPs embedded in polymer matrix and free TiO_2 NPs (20 nm)

Sample Characterization: TEM Analysis

Runoff waters from ageing
$PP+TiO_2@SiO_2$

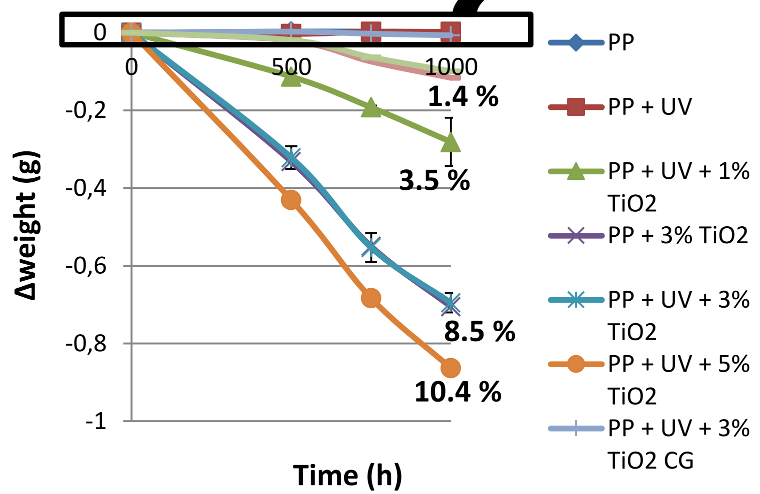


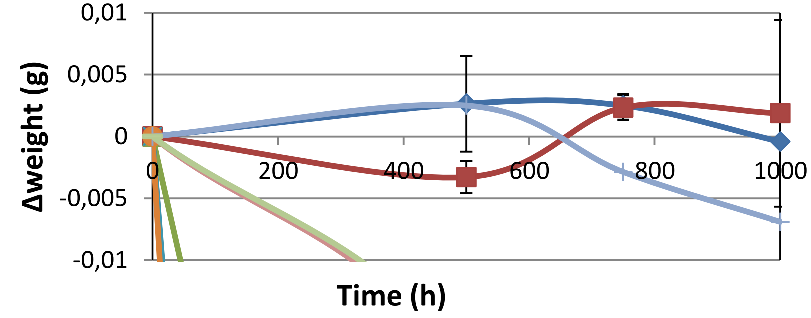
Runoff waters from ageing
$PP+TiO_2@SiO_2$+UV st.



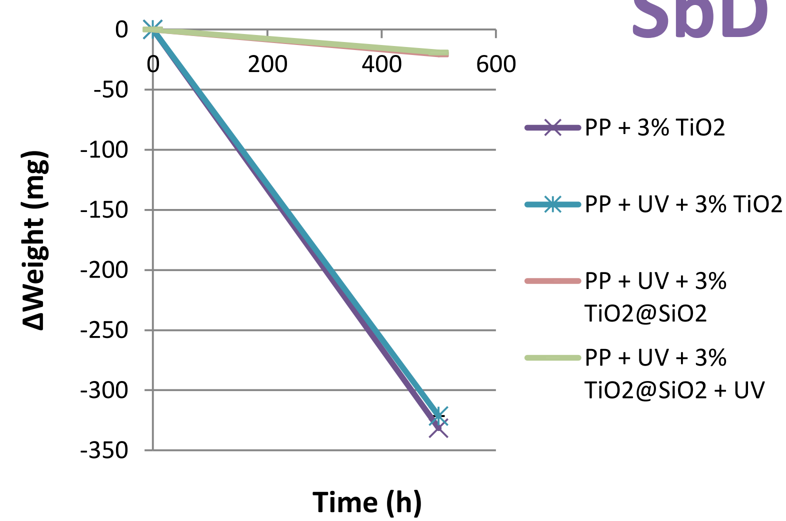
$TiO_2@SiO_2$ NP (25 nm@3 nm) were found on runoff waters during ageing of samples containing UV stabilizer and without UV stabilizer

Sample Characterization: Weight lost analysis



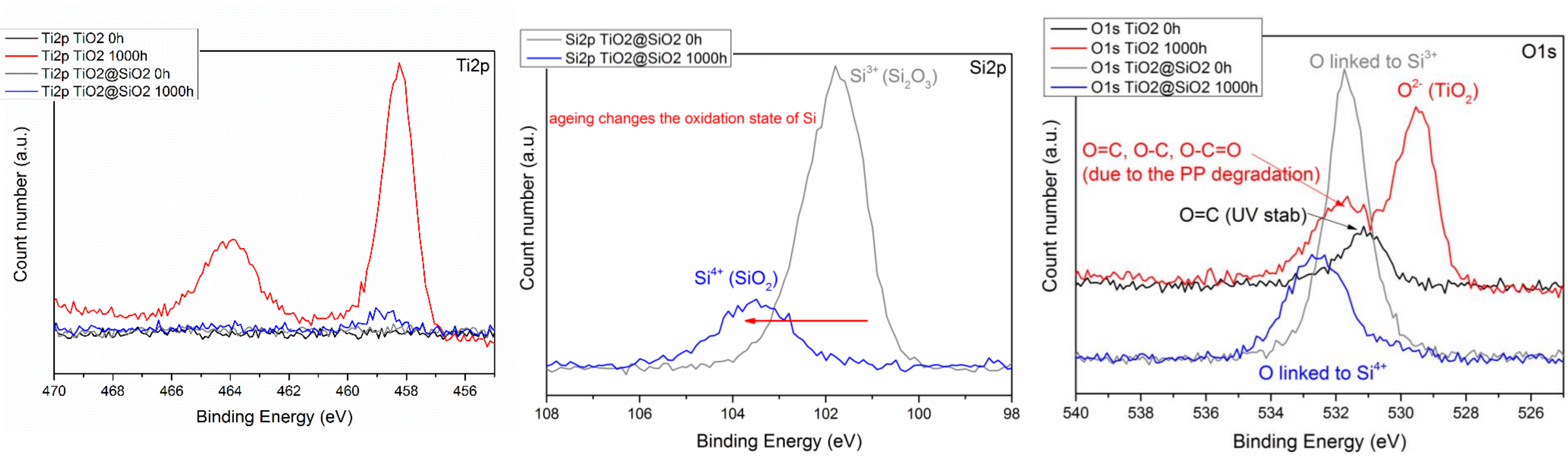


SbD



1. Weight lost could not be observed in polymer samples without NPs
2. Weight lost in samples with TiO_2 (rutile) lower than samples containing TiO_2 NP (anatase)
3. Weight lost could be decreased by using a safer-by-design NP (TiO_2@SiO_2 NPs)

Sample Characterization: XPS Analysis



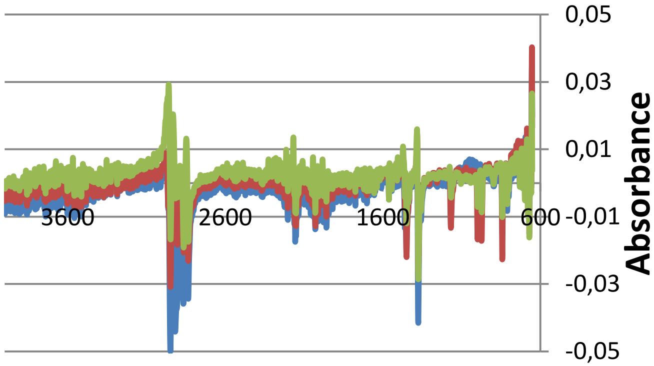
No TiO_2 observed on the surface of both nanocomposites before ageing because they are covered by an organic layer

A great amount of Ti observed after ageing of PP+3% TiO_2+UV stb.

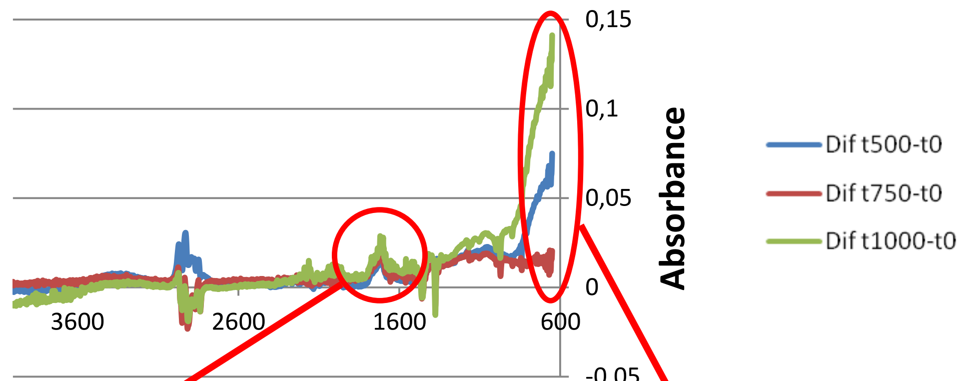
Very small amount of Ti observed after ageing of PP+3% TiO_2@SiO_2+UV sb.

Sample Characterization: FTIR-ATR Analysis

PP



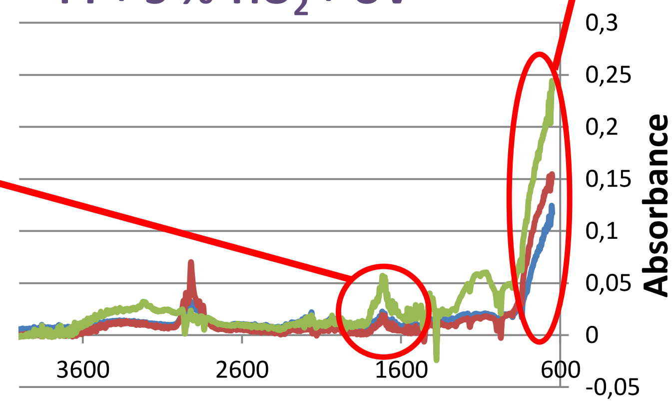
PP + 3 % TiO_2

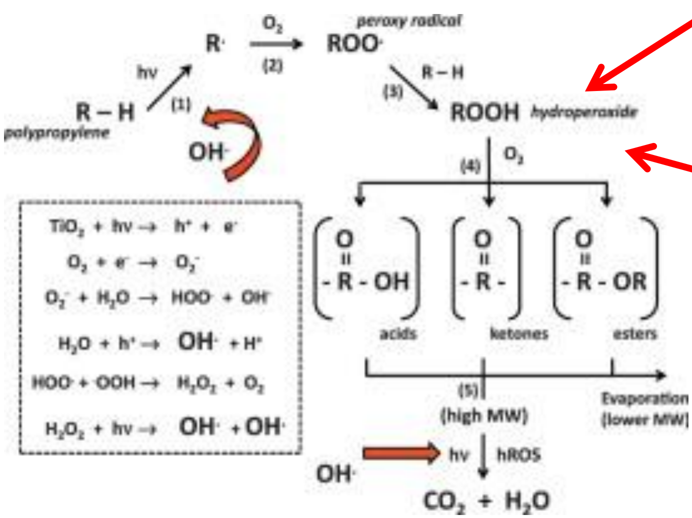


Polymers with TiO_2 NPs exposed to UV light show surface degradation

TiO_2 NP accumulation on the surface with ageing

PP+ 3 % TiO_2 + UV



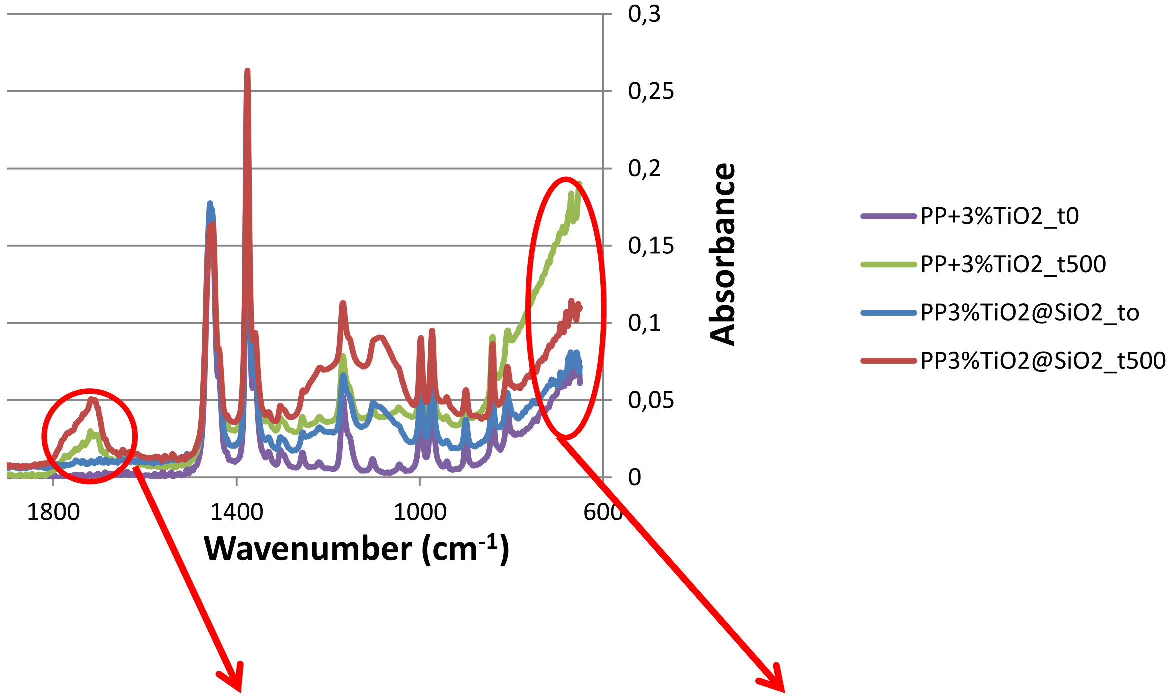


X.L. García Montelongo *et all*, Mat. Res. Bull., **2014**, 51, 56-62

Sample Characterization: FTIR-ATR Analysis

Safer-by-design NPs

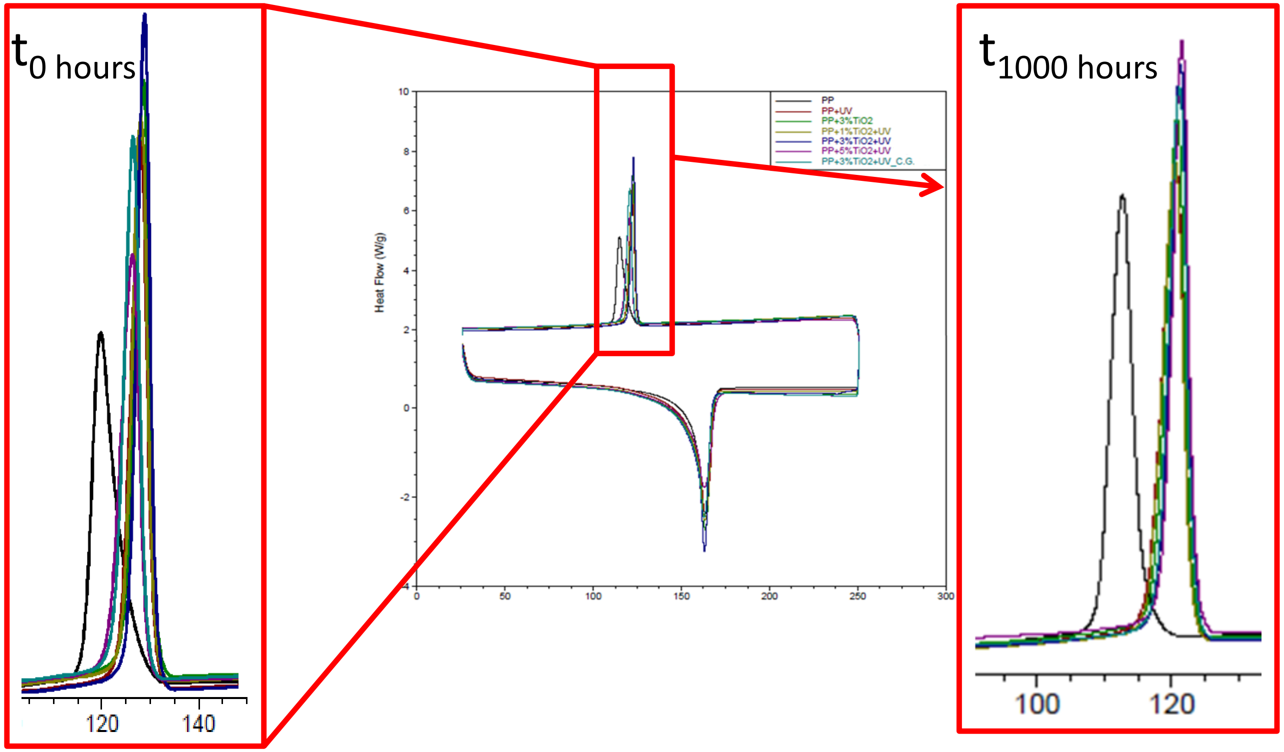
Safer-by design TiO_2 NPs ($TiO_2@SiO_2$, 25 nm@3 nm): Degradation of the polymer occurs (photo-oxidation can be observed) however the material release decreases compared to uncoated TiO_2 nanocomposites

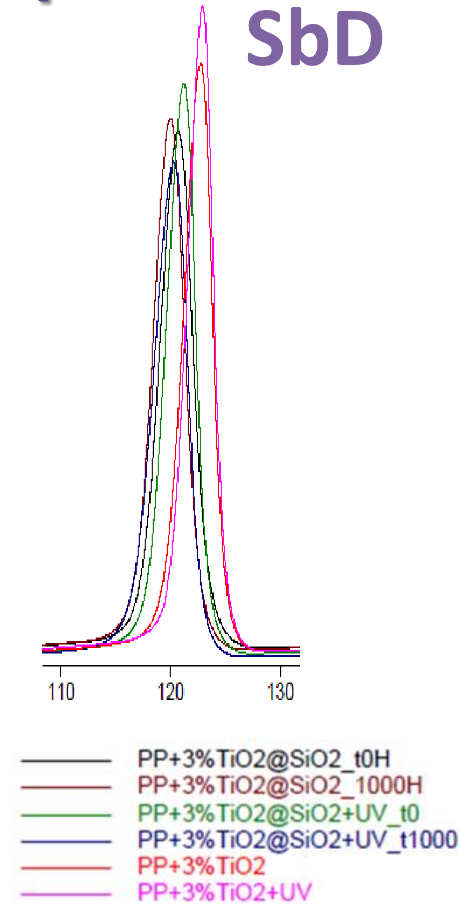


Characteristic photo-oxidation peaks during the ageing process in both nanocomposites

Sample Characterization: Thermal properties- DSC

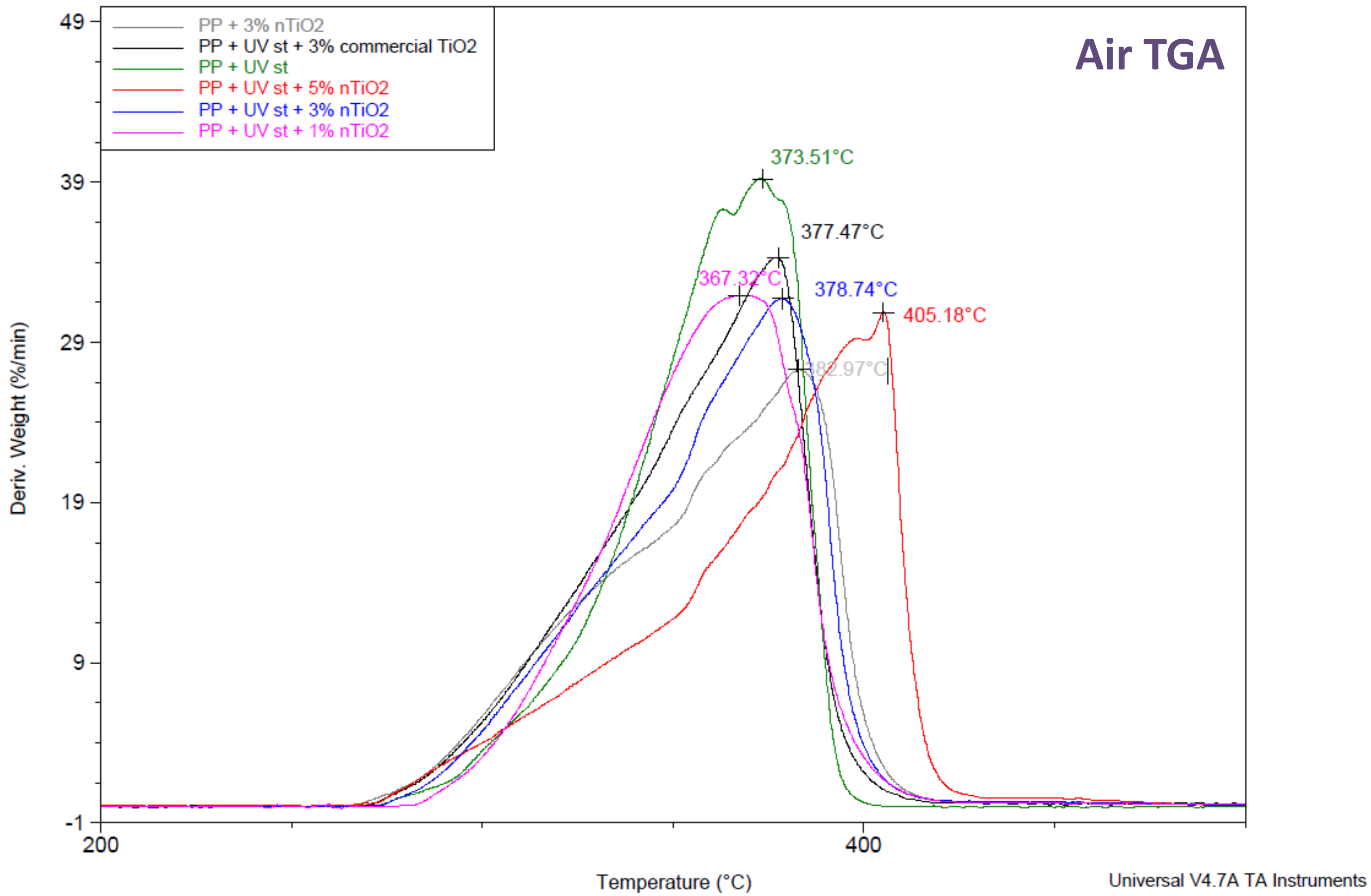
SbD





- Crystallization temperature increases in 10 degrees by adding stabilizers
- The same pattern was found on aged samples
- Crystallization temperature did not changed after ageing nor after implementation of SbD strategies

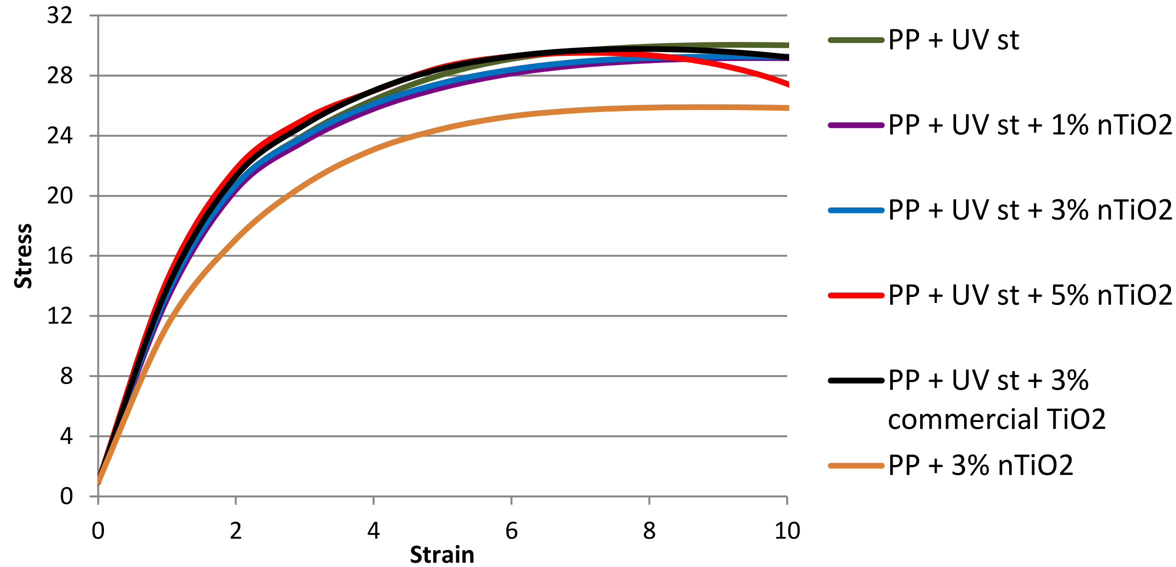
Sample Characterization: Thermal properties- TGA



Protective effect of TiO_2 could be observed

No difference observed between rutile and anatase TiO_2 NPs

Sample Characterization: Mechanical properties



	S.I. Metric	PP + UV st.	PP + UV st. + 1% TiO_2	PP + 3% TiO_2	PP + UV st. + 3% TiO_2	PP + UV st. + 5% TiO_2	PP + UV st + 3% commercial TiO_2
Elong. @ break	%	>100	>100	>100	>100	80	54

- Elongation to break is reduced when the amount of TiO_2 reaches 5%
- The use of big particle size (200 nm) reduces the elongation to break

Summary & Conclusions

1- PP nanocomposite samples with different TiO_2 fillers were aged and characterized

2- Analysis of released materials from different TiO_2 nanocomposites showed that TiO_2 phase plays an important role on release due to photo-oxidation

3- Safer by Design strategies were applied in order to reduce polymer degradation and subsequent reduction of release materials

- Decrease of polymer degradation by using TiO_2@SiO_2 NPs
- Degradation of the polymer occurs but less material is released during the ageing process (further studies are in progress to fully understand the different mechanisms)

4- Polymer mechanical properties improve by decreasing the particle size, however the coated NPs do not show a significant effect in the mechanical properties

Acknowledgments

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GUIDEnano Tool presentation during 5th International Conference NANOSAFE 2016

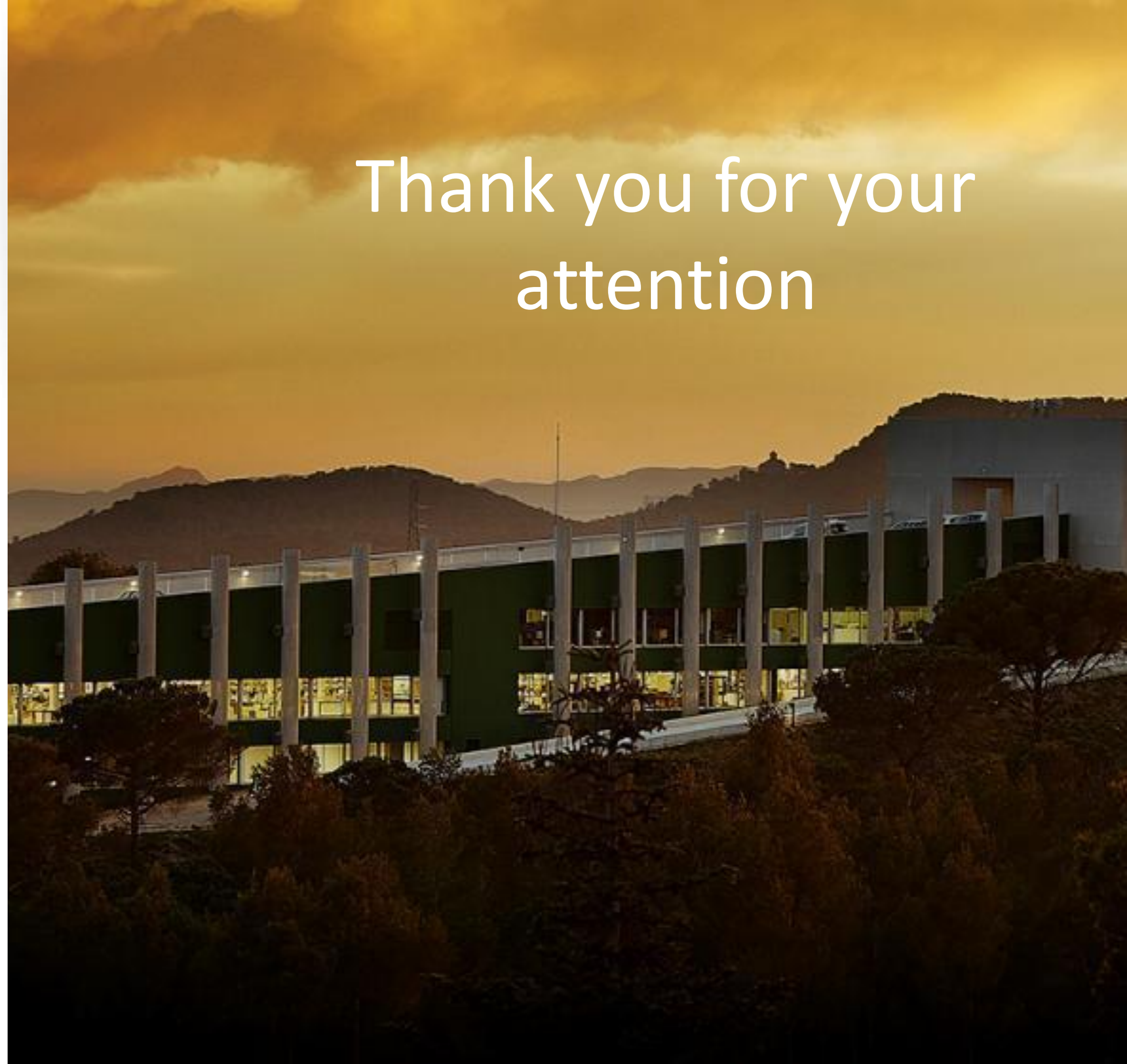
(November 10th, 08.00h-12.00h, Room: Chrome 1)

GUIDEnano will present the latest version of its risk assessment Tool in a satellite event. Industries, regulators, insurance companies, consultants, and researchers working with nanomaterials are invited to participate.

The Tool has the capacity to guide users smoothly through the nanomaterials risk assessment facilitating decision-making and safe-by-design processes to different stakeholders.

The potential of GUIDEnano Tool will be shown with examples of case studies from industries involved in the project working with nanomaterials.

Thank you for your attention



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