COST Action FP1405 Meeting

"Existing technologies and current developments in active and intelligent packaging"

Paper Packaging based on Photoactive Inorganic Nanoparticles: activity and influence on End of Life options

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WG3 - LCA/ Sustainability issues, health and safety

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STAZIONE SPERIMENTALE CARTA, CARTONI E PASTE PER CARTA

15-16 September 2015

Development of Antibacterial Paper Packaging

Potential targets:

- Food packaging: fruits, vegetables, flowers

- Degradation caused essentially by bacteria, fungi and contaminants:
  - Bacillus, Enterobacter, Lactobacillus, Leuconostoc, Pseudomonas, Sarcina, Staphylococcus, Streptococcus, Candida, Saccharomyces, among other species.

- Medical packaging: preventing medical cross contamination

<u>Aim:</u>

Increase shelf-life:

- prevent product spoilage by antimicrobial effect

Maintain product quality and safety.

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Outline

Studies on the antibacterial effect of TiO_2 NPs coated paper

- Influence of the storage conditions
- Hydrophilic vs. Hydrophobic paper

Development of photo-active TiO_2/NFC coating formulations

- Direct Mixture vs. LbL approach
- Antibacterial activity

Industrial Pilot trial at Multipackaging Solutions (UK)

- Development of an active overprint varnish formulation
- Antibacterial assessment of paper-based packaging with ZnO active nanoparticles

Considerations on the impact on End of Life options

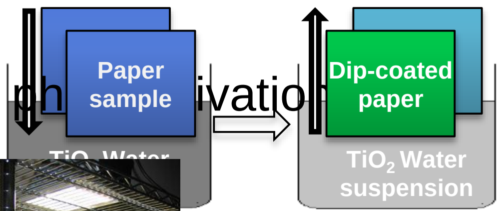
- Biodegradability
- Recyclability

Methodology

- Functionalization of the paper surface with TiO_2 NPs
  - Dip-coating: physical adsorption of inorganic nanoparticles
  - Rod-coating: previous inclusion of nanoparticles in the NFC

Sample	Grammage ($g.m^{-2}$)	Cobb60 ($H_2O.m^{-2}$)
BK	120	74.45
BPK	300	8.42

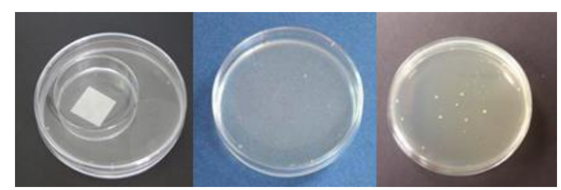
- TiO_2 ph ivatio



4 h of exposition:
- solar lamp (GE ARC70/UVC/730 - 6000 lux)

- Antibacterial activity

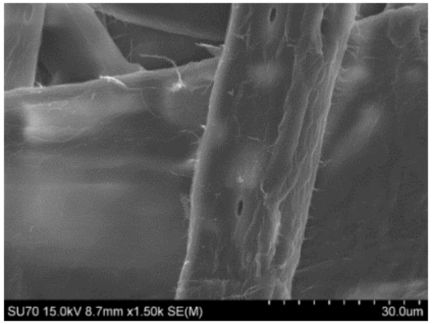
Based on AATCC Test Method 100-1998.



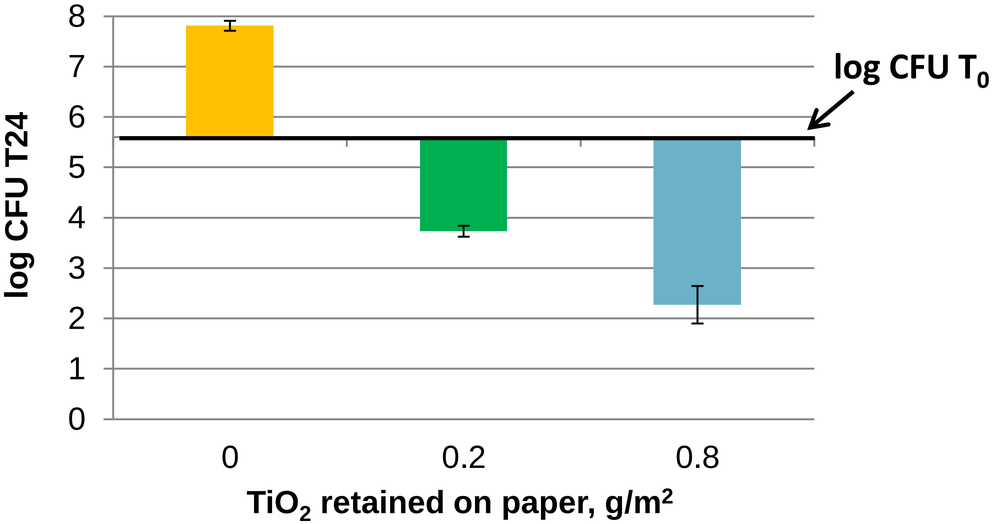
Antibacterial effect of TiO_2 NPs coated paper

- Bleached Kraft paper - BK

S. aureus	log T_o = 5.6
Sample	R
BK1	4.1
BK2	5.5



Reference - BK



Antibacterial activity: Influence of the storage conditions

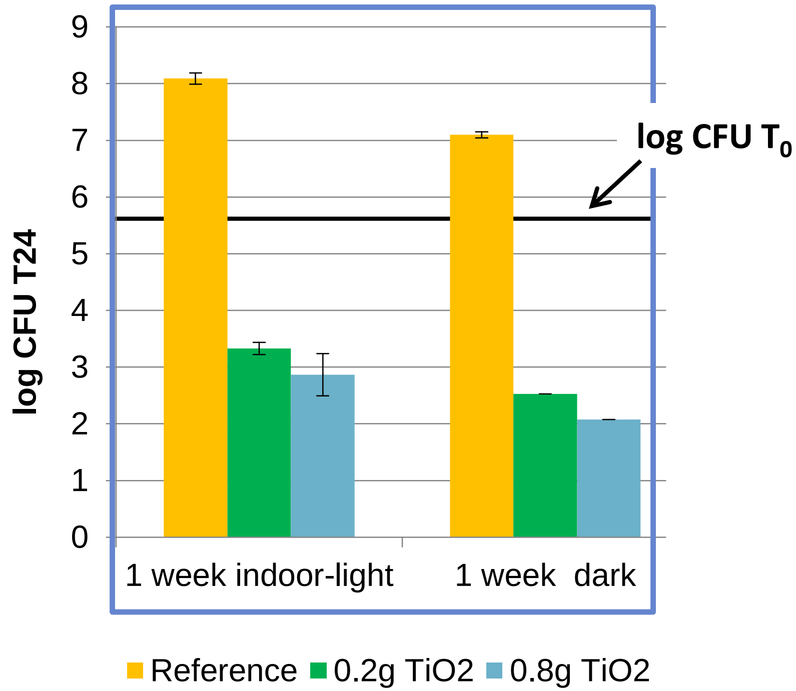
- Influence of the storage conditions over time: Indoor-light *vs.* dark

1 week

Bactericidal effect for both indoor-light and dark conditions.

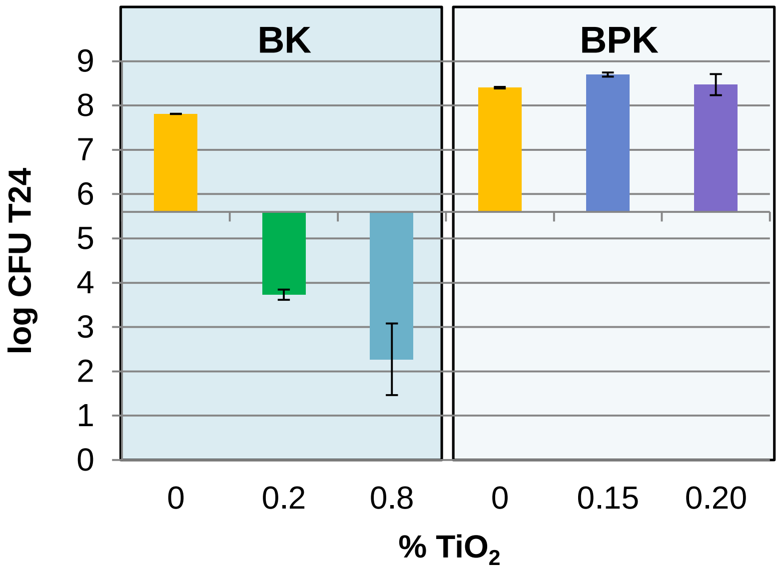
3 weeks:

The bactericidal effect continues and is independently of the storage conditions.



Antibacterial activity: Hydrophilic vs. Hydrophobic paper

- Bleached Kraft paper (BK) *versus* Bleached pre-coated Kraft paper (BPK)



S. aureus	log T_o = 5.6
Sample	R
BK1	4.1
BK2	5.5
BPK1	0
BPK2	0

BPK - Drawbacks

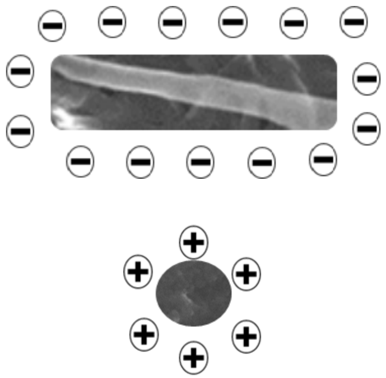
Lower Cobb 60 – hydrophobic paper

Non-homogenous coating

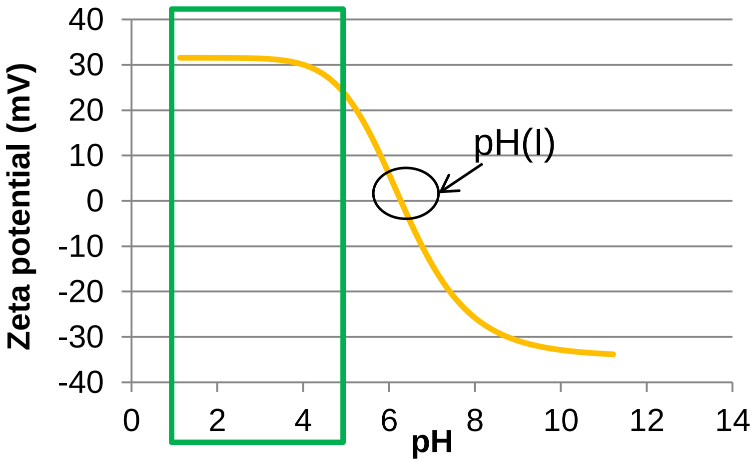
Development of photo active TiO_2/NFC coatings

Advances in the use of NFC as a binder for rod-coating formulations

- NFC – nanofibrillated cellulose
  - Negatively charged surface
- NPs suspension
  - Initial conditions: 6%TiO_2, pH = 1
  - Positively charged



<u>Electrostatic behaviour of the NPs suspension</u>

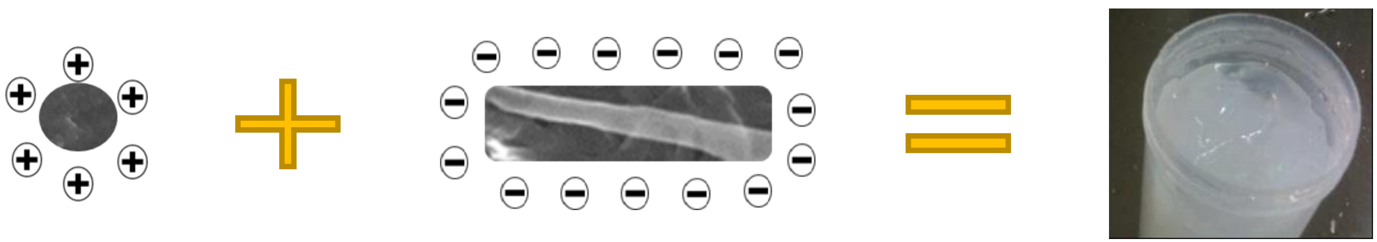


TiO_2 NPs suspension is stable only at positive charge.

TiO_2/NFC coating formulations

- Direct mixture

Deposition of inorganic nanoparticles onto the NFC fibres surface



IDEA: Increase the retention of NPs on NFC

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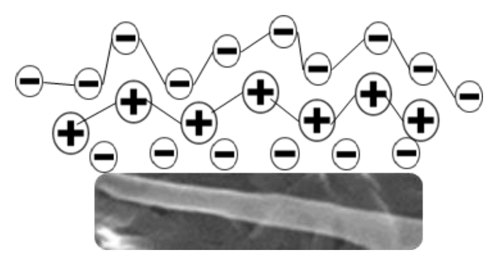
- Layer-by-layer assembly - LbL approach

By modification of NFC:

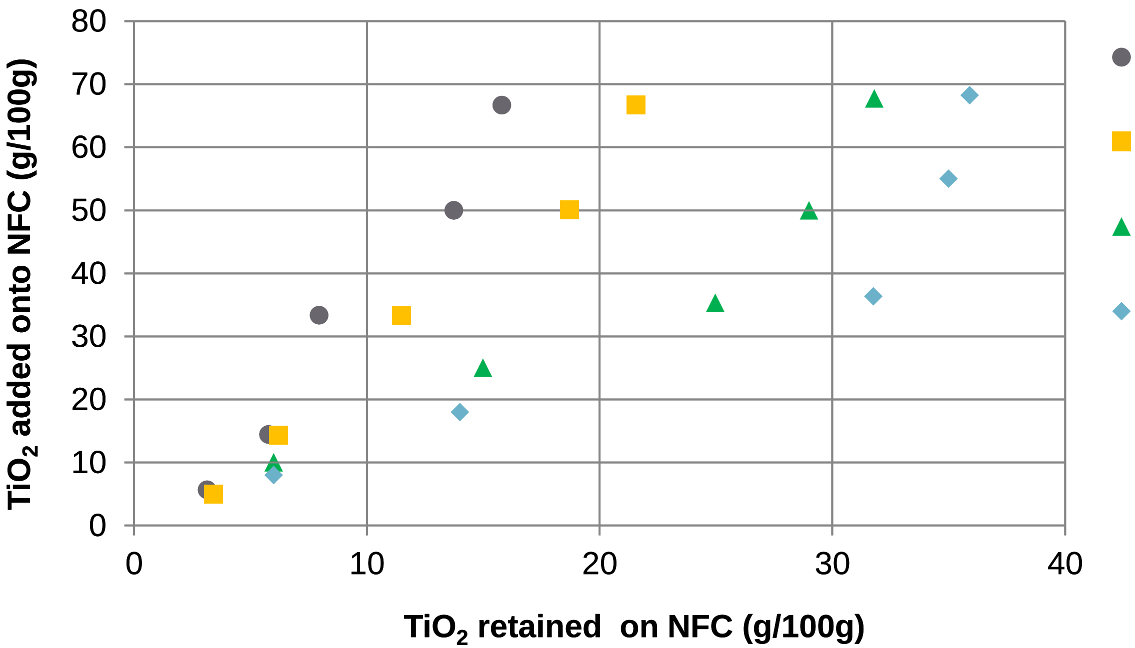
1. Polycation solution (PDDA)
2. Polyanion solution (PSS)

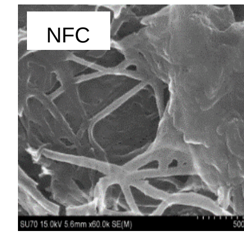


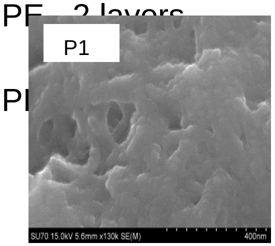
Increasing the negative charge of NFC

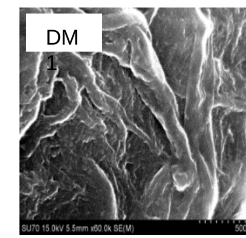
Direct Mixture vs. LbL approach: retention efficiency

- Relation on the %TiO_2 retention by NFC









- DM formulations: just 25% of retention efficiency;
- PE type formulations presents a better efficiency for higher quantities of TiO_2 added to NFC;
- PE-3 layers shows the highest electrostatic interaction with a maximum of 90% of NPs grafted onto NFC.

Antibacterial activity

- BPK paper samples rod-coated with TiO_2 /NFC coating formulations

S. aureus	log T_o = 5.6
Sample	R
0.7 g TiO_2	1.8
4.1 g TiO_2	2.7

Bacteriostatic effect

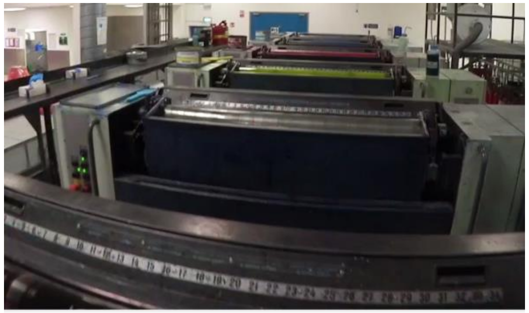
- Inhibition to bacterial growth (≈ 2 log bacterial reduction) is verified on paper surfaces with 0.7 g of TiO_2 NPs per square meter;
- Antibacterial effect increases for higher concentrated samples.

✓ Possibility to develop contact active surfaces

Industrial Pilot trial at Multipackaging Solutions

- Development of an active overprint varnish formulation based on ZnO nanoparticles

  ↳ flexography printing



Target
Medical packaging to prevent cross contamination in hospitals

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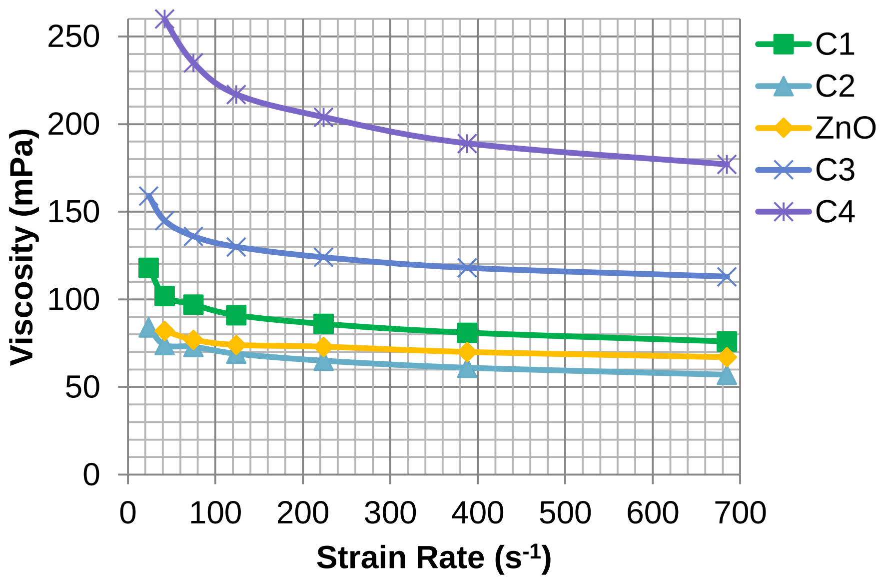
Development of the overprint varnish

Industrial trial – considerations

- Inorganic nanoparticles were chosen due to their commercial availability and good compatibility with industrial needs (e.g. absence of odour);
- TiO_2 was not compatible with the commercial varnish used at the industrial installation;
- ZnO was found compatible with the commercial varnish and had the advantage of being less sensitive to photo activation (dual antibacterial mechanism).



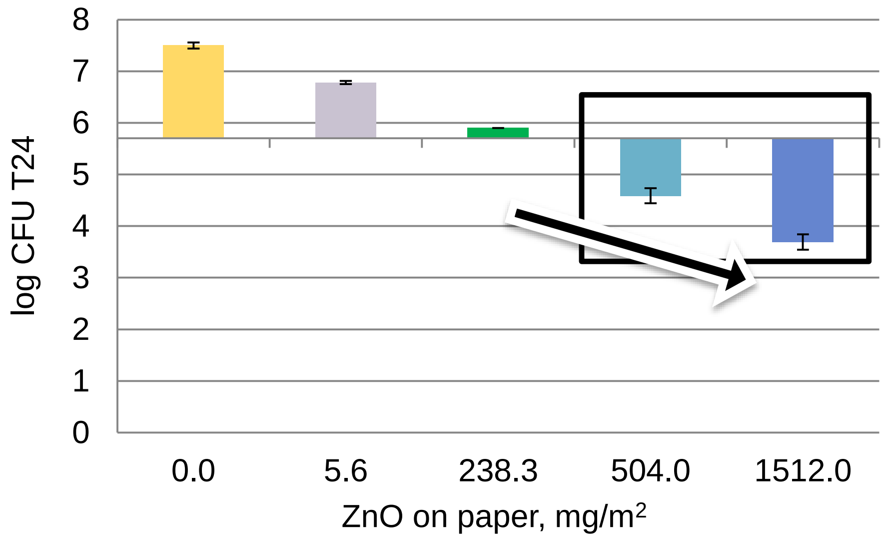
Relatively good viscosity behaviour when up to 10% of the varnish was replaced by ZnO formulation.

Antibacterial activity

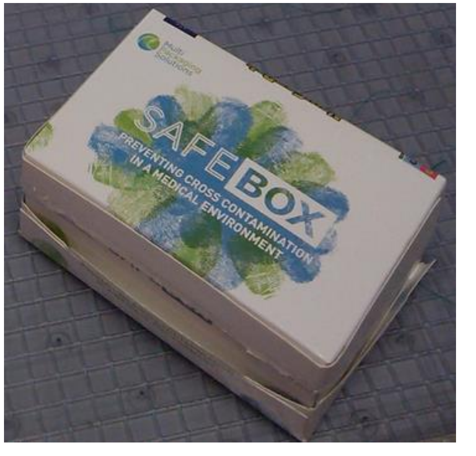
- Paper-based medical packaging with ZnO active nanoparticles - *SAFEBOX*

Poor bacteriostatic effect (R<1)

On the other hand!



S. aureus	log T_o = 5.8
Sample	R
5.6 mg	0.7
238.3 mg	1.6
504.0 mg	2.9
1512 mg	3.8



- Promising results for packaging with higher amounts of ZnO NPs

  ➡ Bactericidal effect

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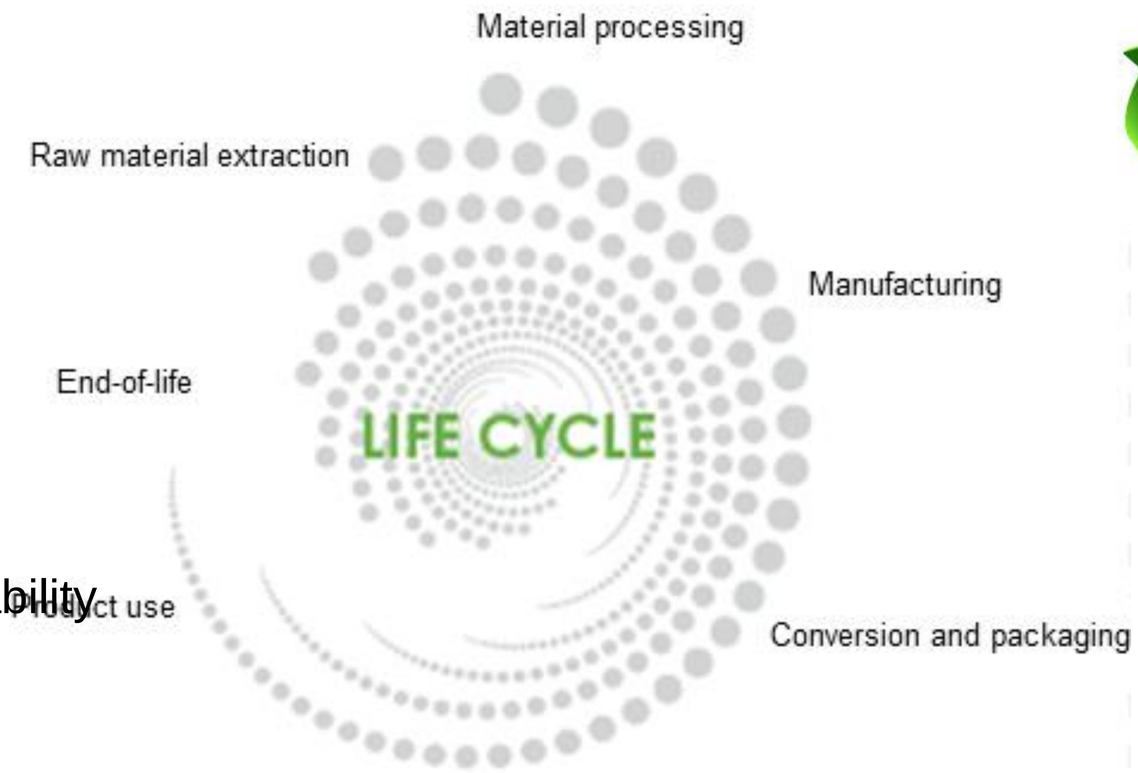
Considerations on the impact on End of Life options

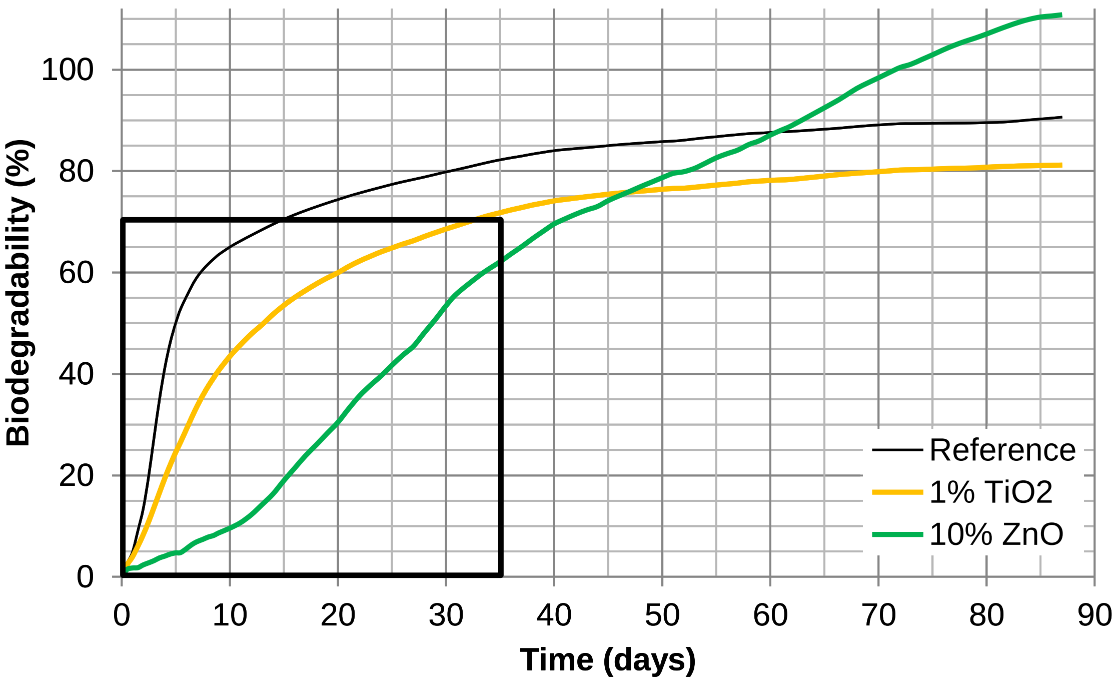


- Biodegradability
- Recyclability

Biodegradability

Tested according to ISO 14855-1:2012 standard

Does the nanoparticles affects the Biodegradability??



TiO_2 coated paper vs. reference:

- similar kinetic behaviour;
- lower degradation rate;
- final degradation rate almost reach the 90% pass level.

ZnO paper samples:

- clear delay in starting the degradation phase;
- after 10 days, the degradation rate increases more rapidly;
- reach a final degradation rate of more than 100% - normally related to the excessive production of CO_2 on the compost (priming effect).

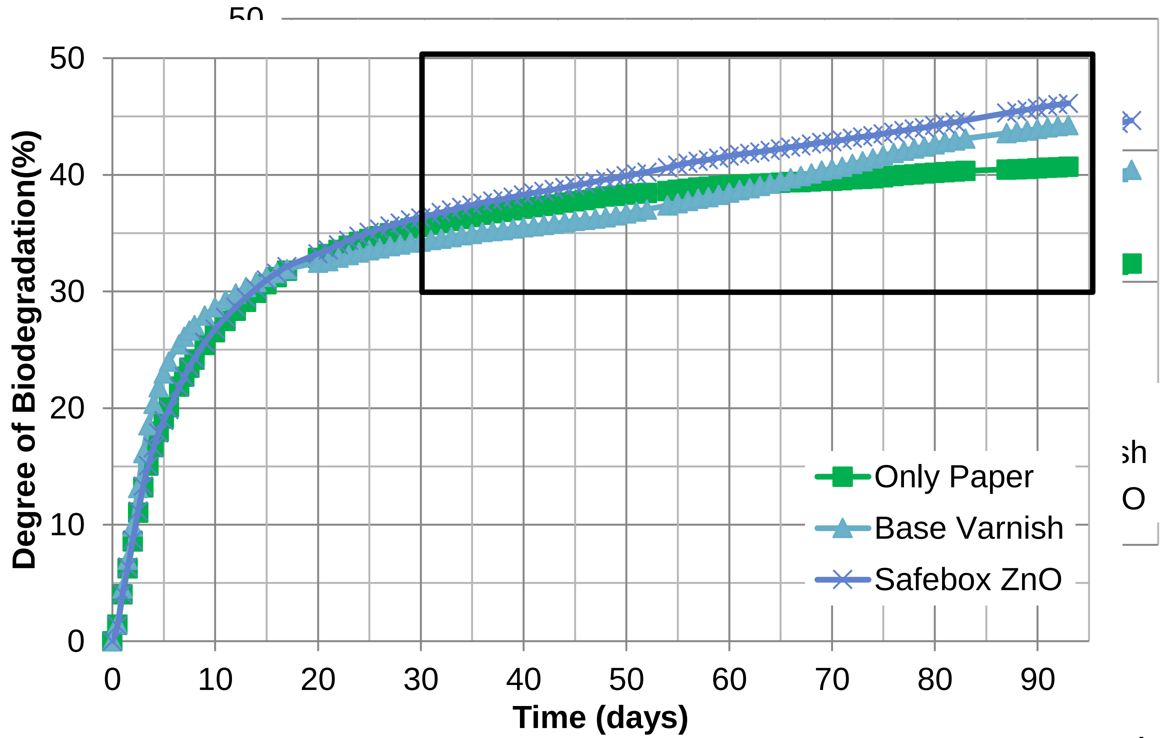
The Biodegradability behaviour maybe due to:

- Concentration of NPs
- Type of NPs

The presence of active ingredients do not necessarily prevent the biodegradation of the material, however more experiments should be done to achieve any conclusion.

Biodegradability

Does the nanoparticles affects the Biodegradability??



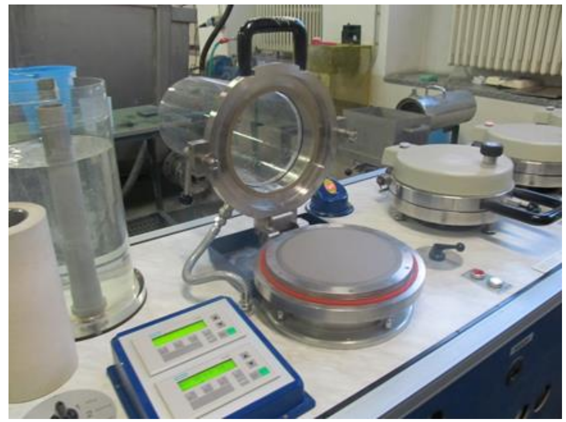
➡ NO SIGNIFICANT DIFFERENCES between treated papers and reference!

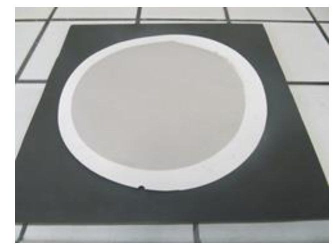
The inclusion of ZnO nanoparticles, at these concentration, does not reduce the final biodegradation

Recyclability of active packaging material

- Test carried out on Kraft paper functionalized with TiO_2 NPs

Aticelca method MC 501-13





To understand where the nanoparticles goes!

- To the water stream, or
- Retained in the fibres?

Sample	TiO_2, g/m^2
Initial sample	**1.47**
Recycled sample	**1.31**

≈ **90%** of TiO_2 NPs stay attached in the cellulose fibres by electrostatic interaction.

Conclusions

- Photoactive TiO_2 nanoparticles can be directly deposited on hydrophilic bleached Kraft paper achieving strong antibacterial contact active surfaces;
- The bactericidal effect last several weeks after activation, under light or dark conditions;
- TiO_2/NFC based coatings formulations can be used for hydrophobic paper samples. They can be developed by direct mixing, however polyelectrolyte-assisted deposition by LBL assembly is a good option to increase retention (90% retention efficiency against 25%);
- The industrial trial performed with an active overprint varnish formulation based on ZnO nanoparticles showed a relatively poor inhibitory effect;
  - Future work will focus on finding suitable varnish components thus increasing ZnO concentration.

Packaging End of Life options

- Recyclability tests proves a very good retention of TiO_2 nanoparticles in the fibres.
- Laboratory tests showed only marginal effect of active ingredients on biodegradability performance.

Thanks for your attention!

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COST Action FP1405
Active and intelligent fibre-based packaging – innovation and market introduction (ActInPak)

ActInPak is a pan European (COST) network of the leading experts in active and Intelligent packaging of over 50 institutes and universities of 28 different countries.

The main objective is to develop a knowledge-based network on sustainable, active and intelligent fibre-based packaging in order to overcome current technological, industrial, and social limitations that hinder the wide deployment of existing and newly developed solutions in market applications.

http://www.cost.eu/COST_Actions/fps/Actions/FP1405

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