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Influence of Nanofillers on the Degradation of a Polyethylene Matrix and Subsequent Release

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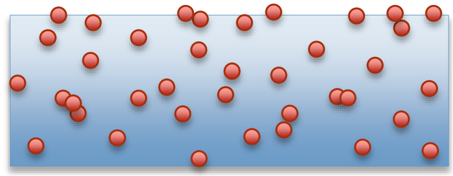
Introduction



POLYMER NANOCOMPOSITES

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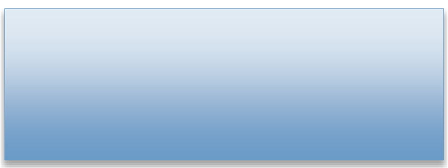
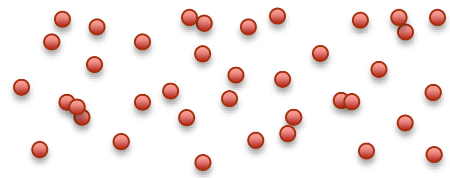


Poylmer matrix

\+



Nanometric filler (= nanofiller)

Risk:
Potential release of nanomaterials from polymer matrix

Improved and/or new properties

- **Possible release scenario** : matrix degradation

chemical alteration ↑ ↑ mechanical action

⇨ **Matrix properties will be a key factor controlling the release.**

Introduction

- **Nanofiller properties can also influence the release:**

Nguyen *et al* (2011):

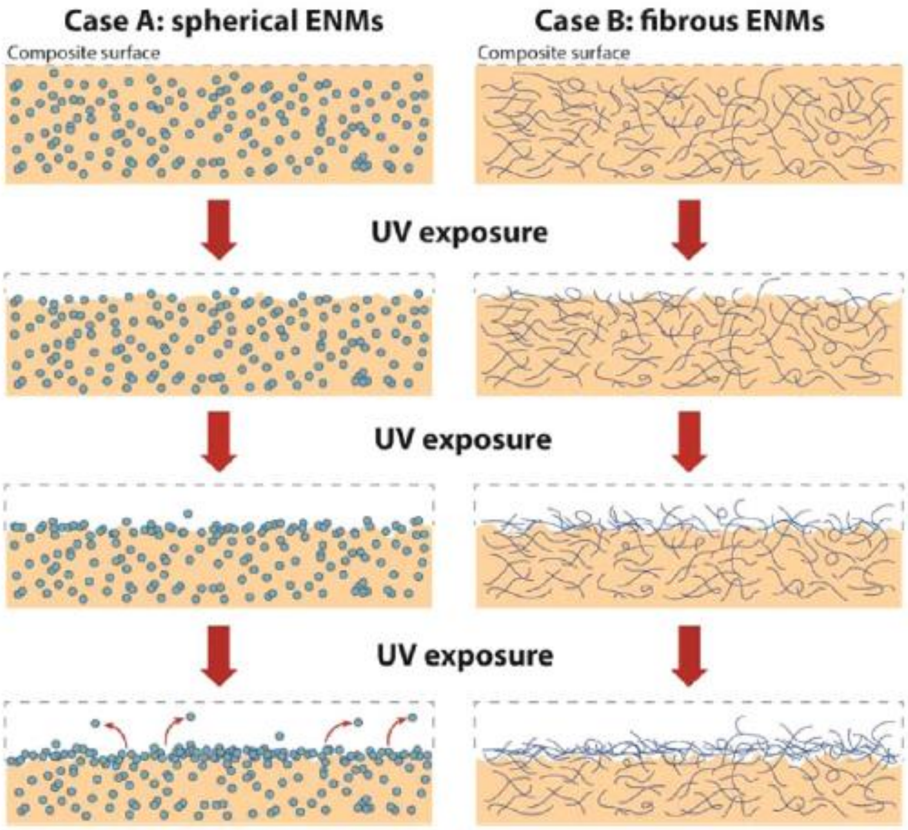
Influence of morphology

SiO_2/epoxy and MWCNT/epoxy nanocomposites

Degradation of epoxy matrix

Accumulation of SiO_2-NPs or MWCNTs at surface

SiO_2-NPs can fall off while MWCNTs remain partly embedded and are not released



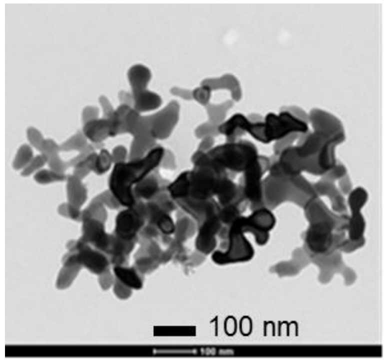
Conceptual model from Duncan (2015), ACS Appl. Mater. Interfaces 7

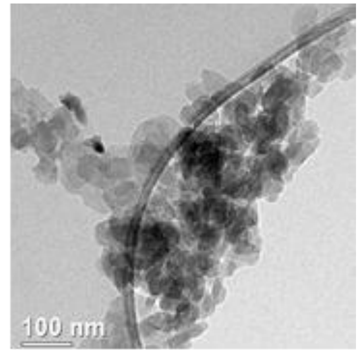
Framework of study : materials

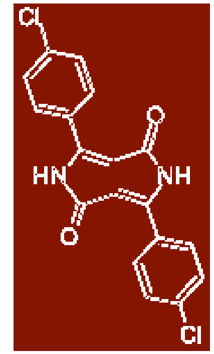
- **2 different nanofillers serving as pigment in a polyethylene (PE) matrix**

Fe_2O_3 nanoparticles
Red 101

Inorganic (Fe, O)
Median particle diameter:
35 ± 20 nm
30 m^2/g *(BET)*





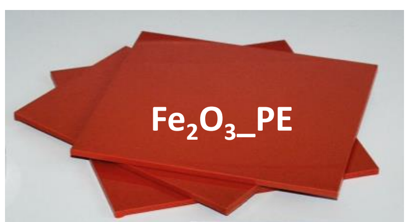


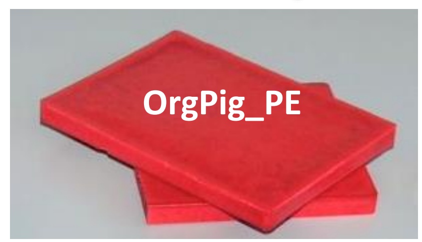
Diketo-Pyrrolo-Pyrrole
Red 254, (DPP)

Organic (C, H, O, N, Cl)
Median particle diameter:
43 ± 14 nm
94 m^2/g *(BET)*

1% — **Incorporated in high-density PE** — 0.2 %

Pure PE (ref)





+ 0.15% UV stabilizer
= OrgPig_PE_UVstab

Final application : car bumpers **PCMA**

Framework of study : artificial weathering

ISO protocol 4892-2A

- **12 weeks** in Atlas Ci 5000 (2016h)
- Exposure to Xe lamp : **50 W/m²**
- High spraying frequency :
  102 min dry / 18 min wet

Release sampling method (Wohlleben et al., 2014)

24h **immersion** in H_2O with 0.5 g/l SDS

+/- 1h sonication

→ Analytical Ultracentrifuge (AUC)

→ Electron microscopy

source: atestor.hu

Characterization of weathered samples :

- ATR-FTIR,

- X-ray computed tomography

+ Adapted ISO protocol on Fe_2O_3_PE

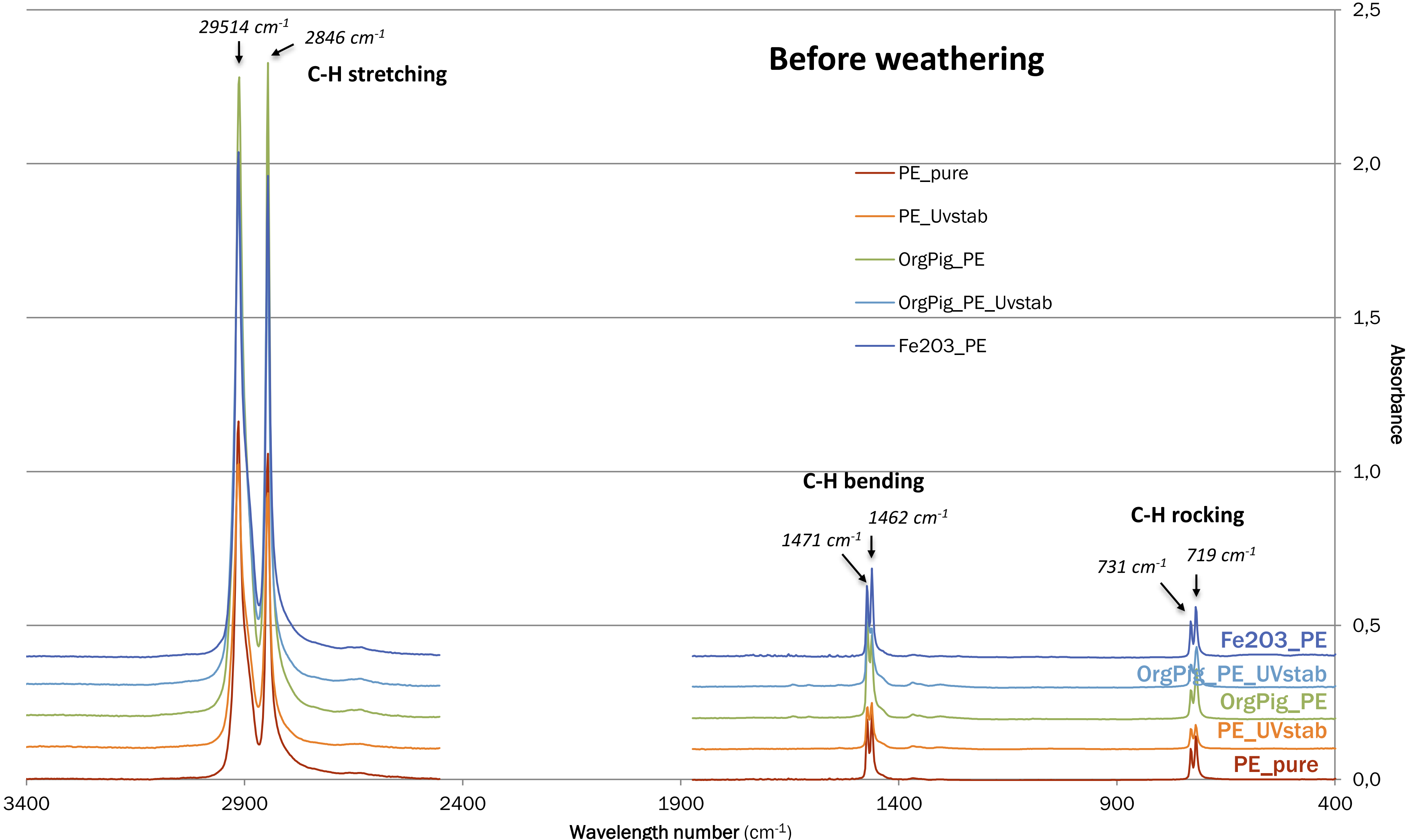
(Suntest XLS+)

- Reduced spraying frequency:
  5 min every 7h + 10 min every 24h

- **Assessment of *in situ* release :**
  - → Sprayed water collected in beakers
  - → Fe release quantified by ICP-MS

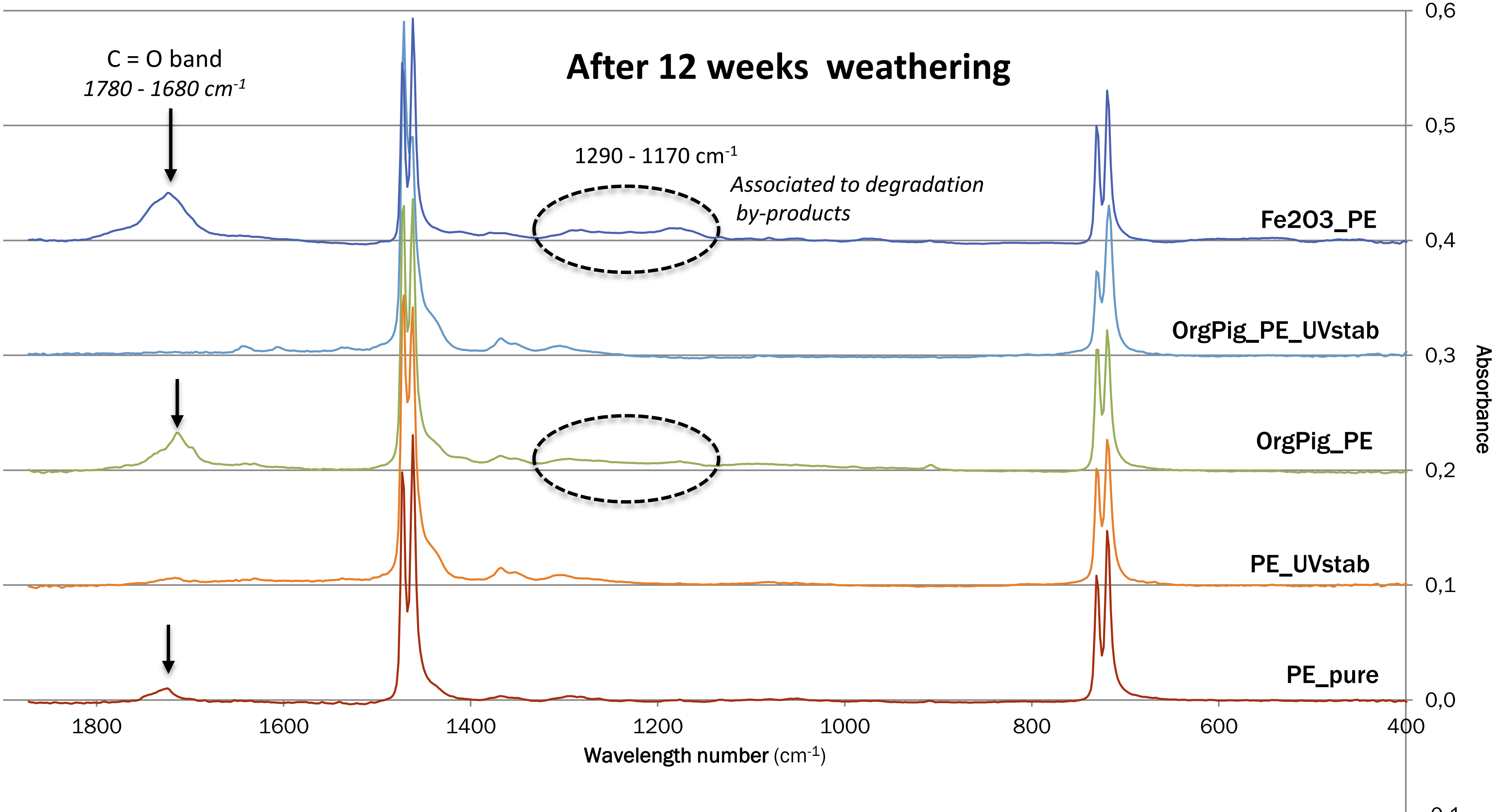
→ *Comparison of degradations and release observed for the 2 pigments*

FTIR spectroscopy



Similar ATR-FTIR spectra on the different materials

FTIR spectroscopy



- Oxidation of the polyethylene matrix for pure PE, OrgPig_PE and Fe_2O_3_PE

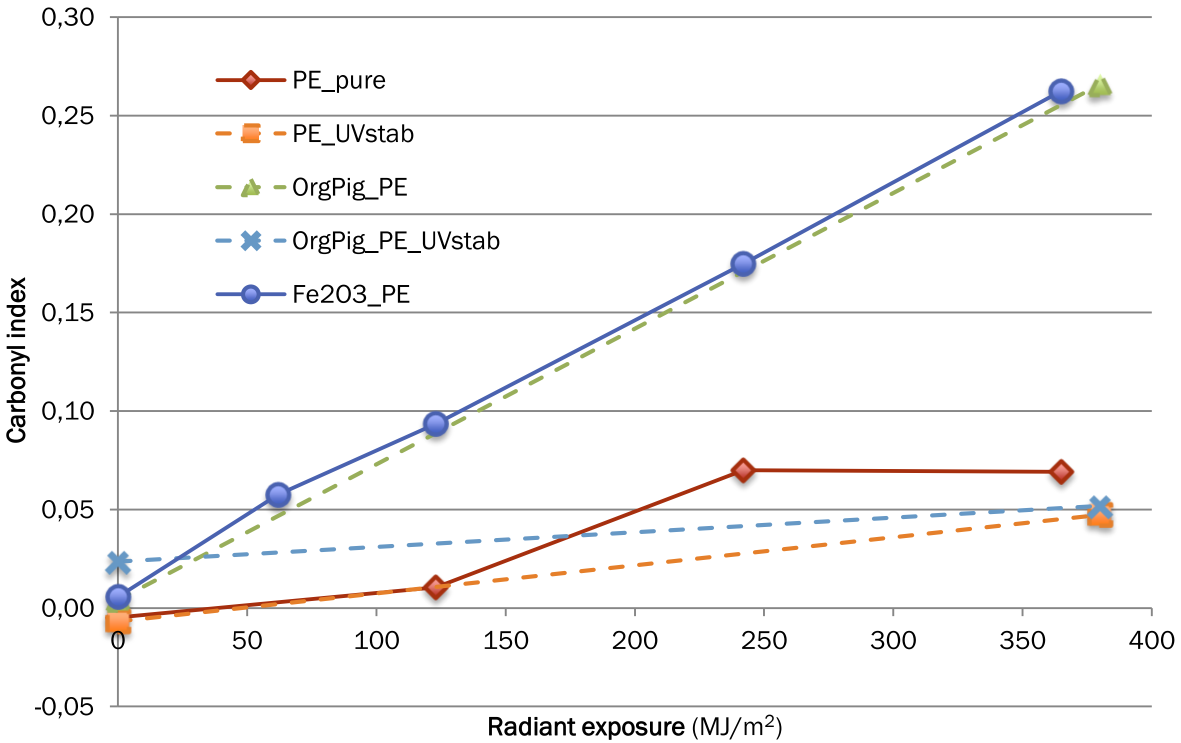
Enhanced in presence of nano-pigments

- Almost unnoticed on UV stab samples → *Good stabilization against photo-oxidation*

ATR-FTIR spectroscopy after weathering

- Comparing PE oxidation on the different samples

Calculation of the Carbonyl Index : $\mathrm{CI} = \frac{A_{C=O}}{A_{719}}$



Low oxidation of pure PE.

Further reduced for PE_UV stab and Org_Pig_PE Uvstab

Linear progress of oxidation in Fe_2O_3_PE

Similar oxidation on Fe_2O_3_PE and OrgPig_PE

↓

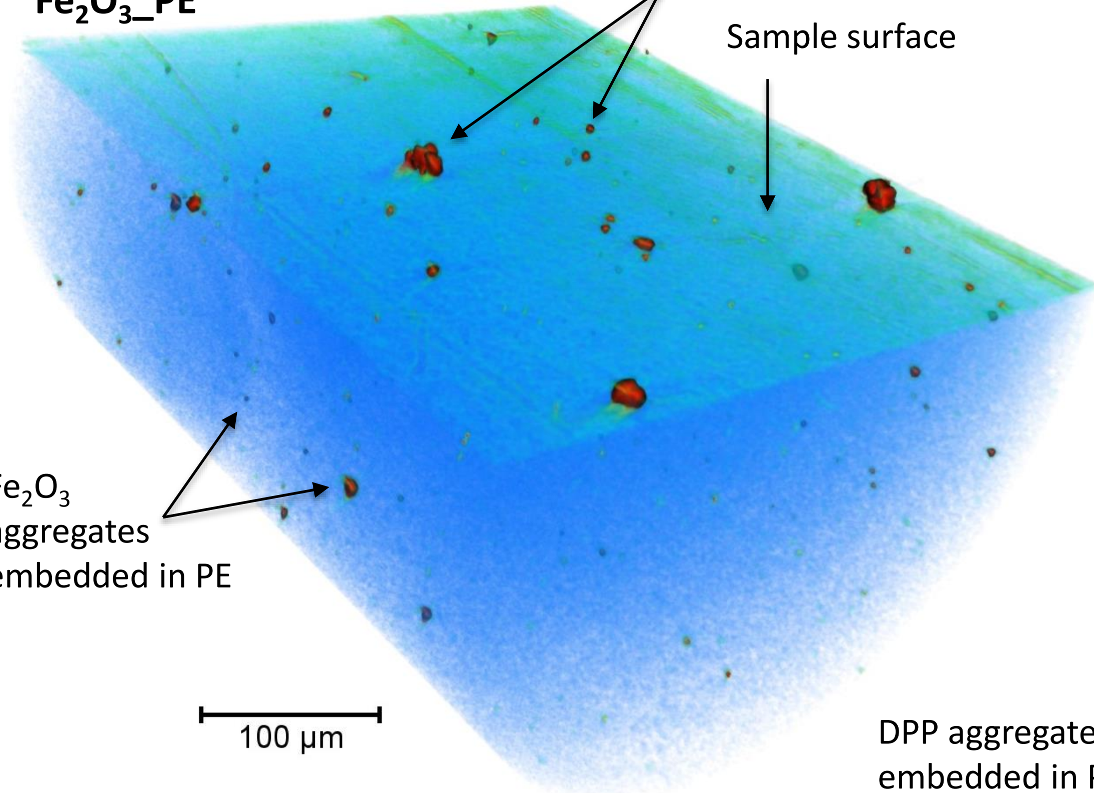
Probably due to their similar absorption of light

(> pure PE)

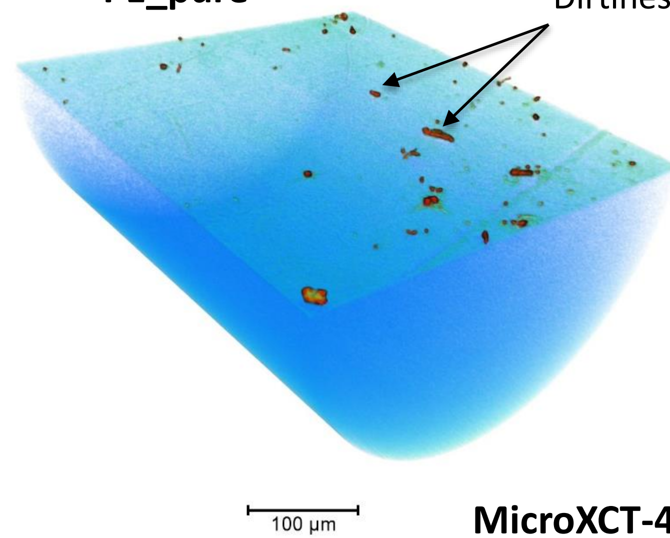
X-ray computed tomography

Before weathering

Fe_2O_3_PE



PE_pure

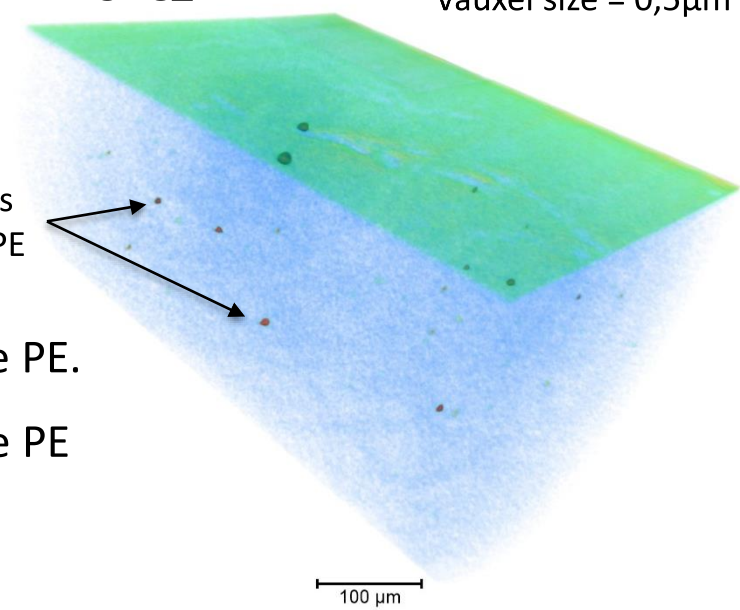


MicroXCT-400

40kV; 10W

Vauxel size = 0,5µm

OrgPig_PE



Fe_2O_3_PE : Aggregates > 1µ visible at surface and inside PE.

OrgPig_PE : Lower number of aggregates, mostly inside PE

Lower content (0.2% vs 1%). Better dispersed?

X-ray computed tomography

NanoID

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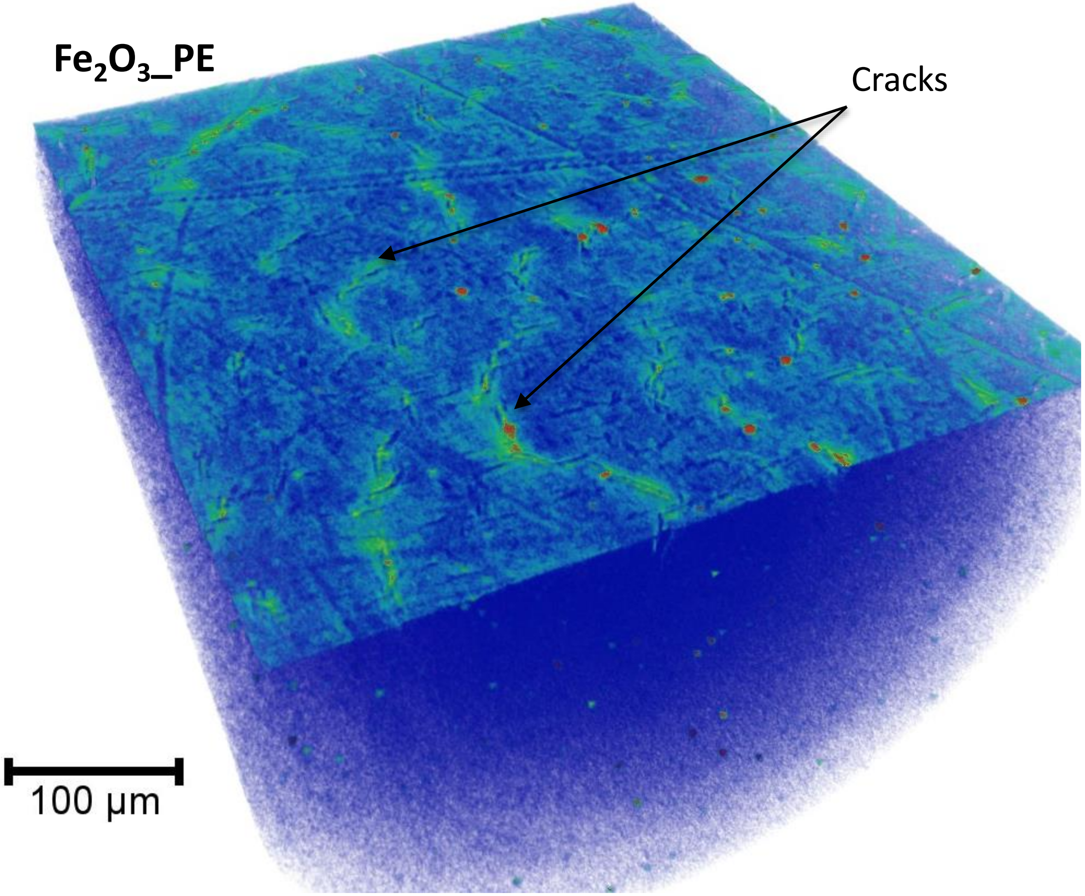
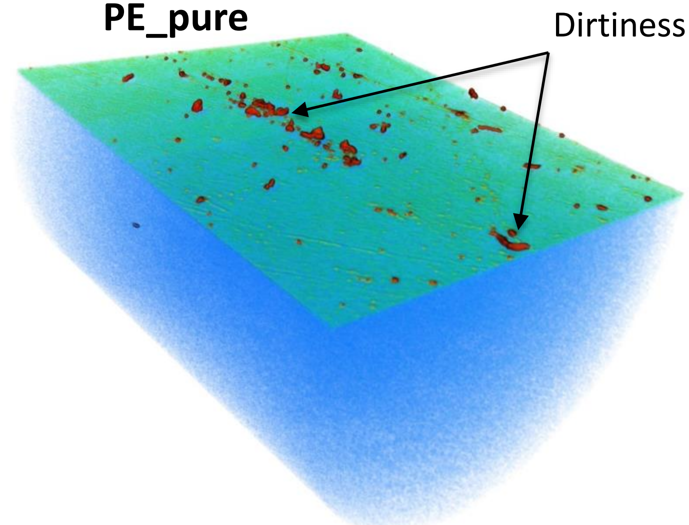
After 12 weeks weathering





PE_pure

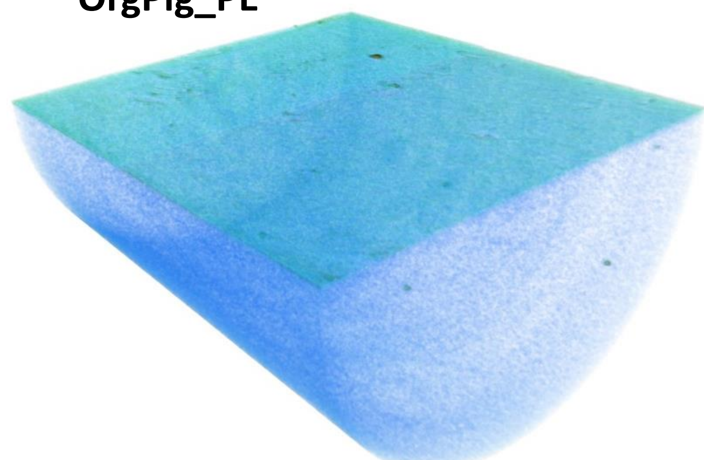
100 µm

MicroXCT-400

40kV; 10W

Vauxel size = 0,5µm

OrgPig_PE



100 µm

No significant change on pure PE or OrgPig_PE.

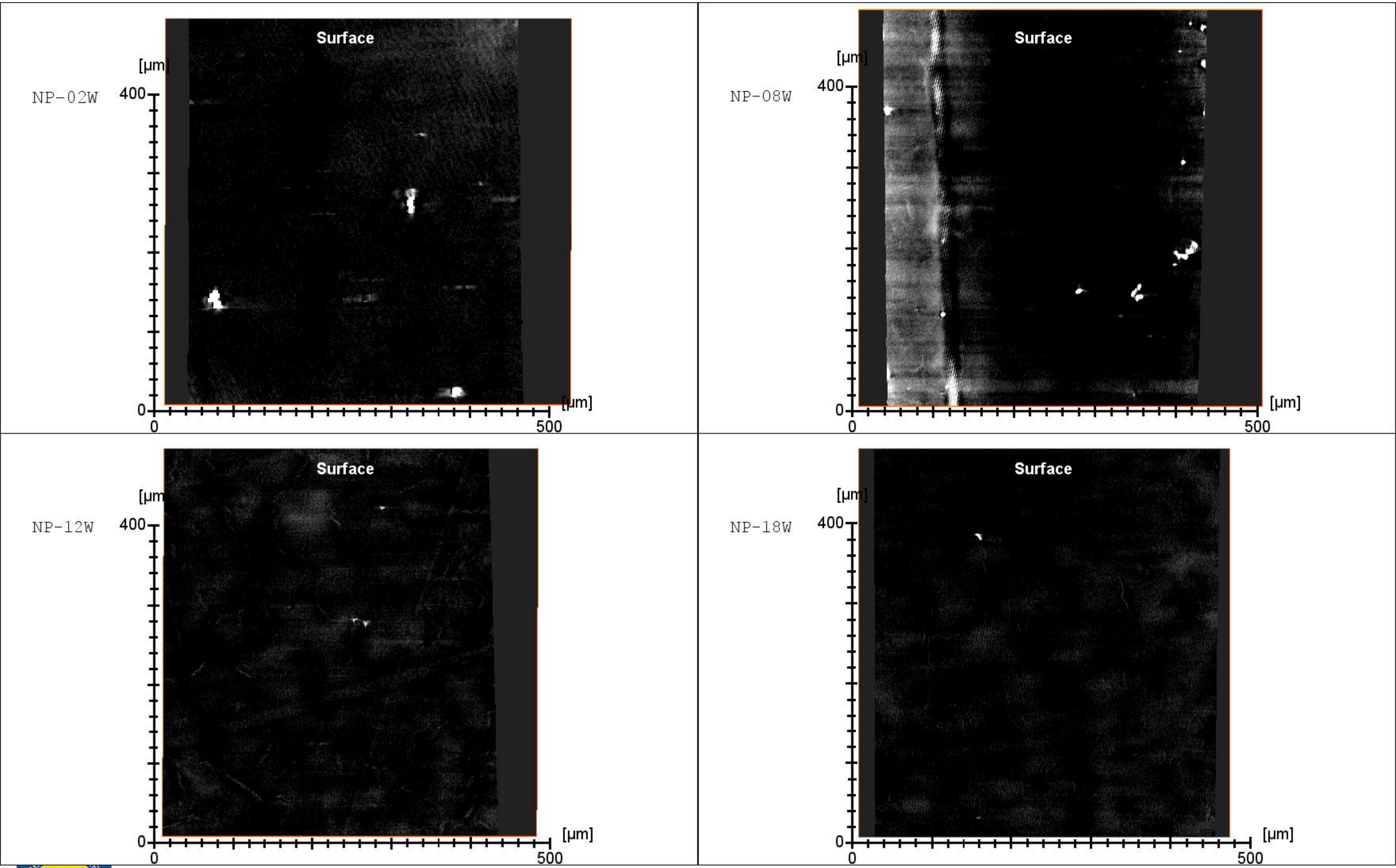
No accumulation of ENMs at sample surface

Fe_2O_3_PE : cracks after 8 weeks weathering.

Fe_2O_3 aggregates in cracks

CEREGE

X-ray computed tomography



↗ number, ↗ length and ↗ depth of cracks with aging.

Nanofiller release from PE

Release during weathering

- **Fe_2O_3_PE**
  - Fe detected in « rain » waters for both Fe_2O_3_PE and pure PE

    ➪ *Contamination prevents a reliable quantification of release*
  - **Loss of mass**

  After 12 weeks:
  - **4,4 mg** on Fe_2O_3_PE *(0,16% initial mass)*
  - **1,9 mg** on PE_USE *(0,07% initial mass)*

    → *Volatilization of PE*

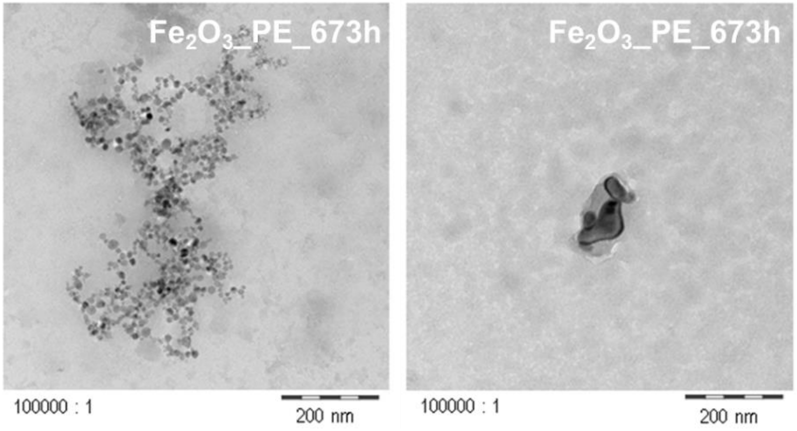
  → ***60.4 ± 1.5 mg/m²*** *Fe_2O_3 not embedded anymore in PE?*

- **OrgPig_PE**

  Not determined

Release during immersion

- **Fe_2O_3_PE**
  - No significant difference between pure PE and Fe_2O_3_PE
  - **Below LoD of AUC** (10 mg/m²) in all cases
  - Fe-containing fragment observed by TEM



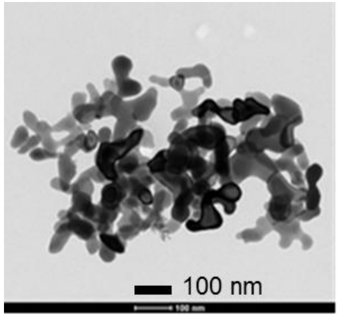
- **OrgPig_PE**
  - No significant difference between pure PE and OrgPig_PE
  - **Below LoD if AUC** in all cases
  - **No fragments** observed by TEM

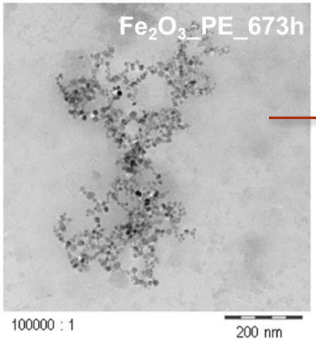
Conclusion

- **Degradation upon weathering**
  - Oxidation of the polyethylene matrix
    - ↳ Enhanced in presence of nanopigments but no specific influence of pigment nature
      Fe_2O_3_PE eq. OrgPig_PE
    - ↳ the use of UV stabilizers limits oxidation
  - Cracking is only observed for Fe_2O_3_PE and mostly around Fe_2O_3_aggregates
    - ↳ Relaxation of mechanical stress in PE matrix

The influence of nanofillers on degradation and release should not be neglected

- **Release of n**
  - **Low in both cases** but cannot be compared on a quantitative basis *(contamination, LoD)*
  - TEM images show evidence for particulate release from Fe_2O_3_PE





↳ Direct release of Fe_2O_3 aggregates at cracks?

→ Transformation?

Hypothesis : Reduction of Fe^{3+} to Fe^{2+} during PE photo-oxidation

But Fe^{2+} unstable

↳ Oxidation and precipitation of $Fe^{3+}OOH$

Different shape and size of released particles with respect to pristine pigments

Thank you for your attention!

Acknowledgments:

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