Modified PHBHHx with Interesting Properties for Food Packaging Applications

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Plastics demand in EU

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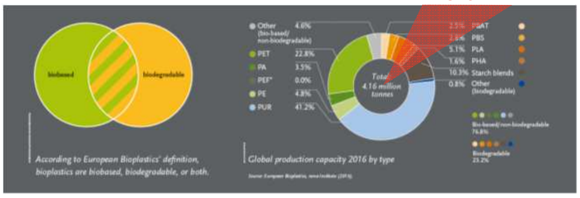
Source: PlasticsEurope (PEMRG)/Consultic/myCeppi, Plastics, the Facts, 2016

Bioplastics

- **Polyhydroxyalkanoates**
  - ✓ Increased resource efficiency
  - ✓ Reduced CO_2 emissions
  - ✓ A wider range of waste treatment techniques due to biodegradability

1.6% PHA



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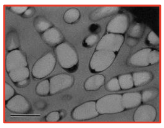
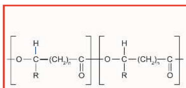
Source: European Bioplastics, Bioplastics - Facts and Figures, 2016

Polyhydroxyalkanoates (PHA)



- **General properties**
  - Bacterially produced from renewable resources
  - Synthesized in many different compositions
  - Thermoplastic (co-)polyesters
  - Semi-crystalline
  - Properties vary greatly with type and amount of co-monomer



n	R group	Monomer type
n = 1	hydrogen	3-hydroxypropionate
	methyl	3-hydroxybutyrate
	ethyl	3-hydroxyvalerate
	propyl	3-hydroxyhexanoate
	pentyl	3-hydroxyoctanoate
	nonyl	3-hydroxydodecanoate
n = 2	hydrogen	4-hydroxybutyrate
n = 3	hydrogen	5-hydroxyvalerate

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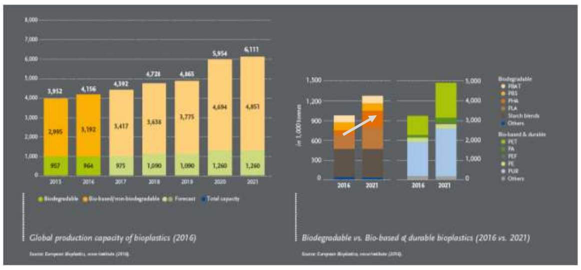
1. Sudesh, K. et al. (2000) Synthesis, structure and properties of polyhydroxyalkanoates: biological polyesters, Prog. Polym. Sci. 25:10
2. Lee, S. (1996) Bacterial polyhydroxyalkanoates, Biotechnol. Bioeng. 49:1

Polyhydroxyalkanoates

✓ **Innovative materials for better performance**



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Source: European Bioplastics, Bioplastics - Facts and Figures, 2016

Objective

Characterization and modification of PHBHHx in order to enhance the applicability of this bioplastic

e.g. in food packaging applications

Modifications:

1. Ultrafine talc
2. Organomodified montmorillonite nanoclay (OMMT)
3. Unmodified and surface-modified zinc oxide (s)ZnO

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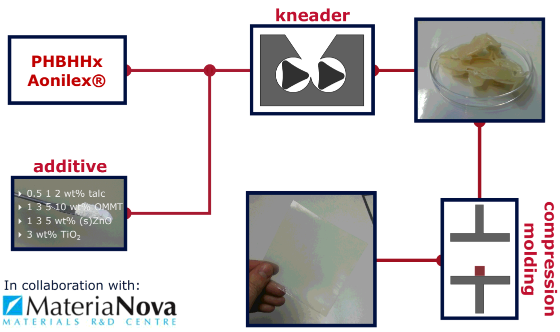
Materials & Methods



In collaboration with: MateriaNova MATERIALS R&D CENTRE

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Evaluation of modifications

Properties of PHBHHx and Aonilex® composites

Thermal stability	Gas permeability
Crystallization behavior	Tensile properties
Color & opacity	UV-VIS transmittance

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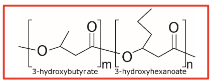
General characterization PHBHHx and Aonilex®

- **Thermal properties**

	T_m [°C]	$T_{d,onset}$ [°C]	$T_{d,peak}$ [°C]	Processing window
PHBHHx	134	291.8	308.1	157
AON	129	290.5	307.0	162

- **Crystallization behavior**

	$T_{c,peak}$ [°C]	ΔH_c [J/g]
PHBHHx	75.0	31.5
AON	76.4	35.4



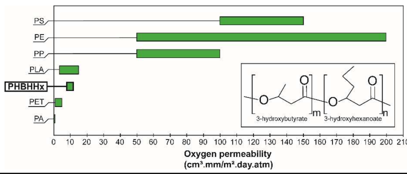
- **Tensile properties**
  - Flexible polymers

9 www.kaneka.be/new-business/kaneka-biopolymer-aonilex

General characterization PHBHHx and Aonilex®

- **Gas permeability**

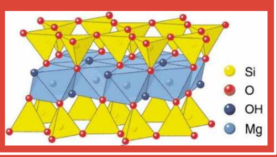
	PHBHHx	AON	
P_{O_2}	8.0 (± 0.2)	9.3 (± 0.4)	[cm³.mm/m².day.atm]
P_{CO_2}	40.5 (± 1.4)	49.0 (± 1.3)	[cm³.mm/m².day.atm]
$P_{water\ vapor}$	1.31 (± 0.02)	1.44 (± 0.04)	[g.mm/m².day]



10 Vandewijngaarden J, et al., **2014**, Gas permeability properties of poly(3-hydroxybutyrate-co-3-hydroxyhexanoate), *Journal of polymers and the environment*, vol. 22, no. 4, pp. 501-507.

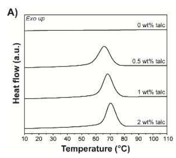
1. Effect of ultrafine talc in PHBHHx composites

- **Talc**
  - Layered phyllosilicate
  - Chemical formula $Mg_3Si_4O_{10}(OH)_2$
  - Often used in polyolefins for reinforcement, enhanced crystallization or as anti-blocking agent
  - 0, 0.5, 1 and 2% wt



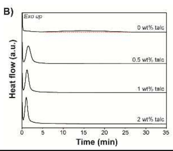
Ultrafine talc acts as nucleating agent in PHBHHx

- **Non-isothermal crystallization** 170°C → -30°C at 10°C/min



Talc content [wt%]	$T_{c,p}$ [°C]
0	n.d.
0.5	65.9
1	68.1
2	70.3

- **Isothermal crystallization** 170°C → 70°C at 45°C/min

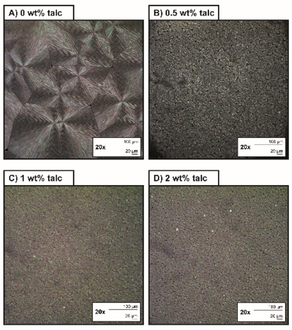


Talc content [wt%]	$t_{1/2}$ [min]
0	15.28
0.5	1.54
1	0.52
2	0.44

12 Vandewijngaarden J, et. All. (2016) "Effect of ultrafine talc on crystallization and end-use properties of poly(3-hydroxybutyrate-co-3-hydroxyhexanoate)", *Journal of Applied Polymer Science*, vol. 133, no. 45.

Ultrafine talc acts as nucleating agent in PHBHHx

- **Spherulite size of PHBHHx**
  - Spherulite size ↓↓
  - Size uniformity ↑↑



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Talc-PHBHHx composites

- **Minor influence on gas permeability**

Talc	PO_2 [cm³.mm/m².day.atm]	PCO_2 [cm³.mm/m².day.atm]	$P_{water\ vapor}$ [g.mm/m².day]
0 wt%	7.9 (± 0.2)	37.0 (± 0.7)	1.27 (± 0.01)
0.5 wt%	9.0 (± 0.7)	41.9 (± 0.4)	1.54 (± 0.09)
1 wt%	8.4 (± 0.2)	39.9 (± 0.9)	1.32 (± 0.04)
2 wt%	7.5 (± 0.2)	38.6 (± 0.7)	1.21 (± 0.05)

- **Only minor influence on other functional properties**
  - 13% increase in Young's modulus (2 wt% talc), tensile strength and elongation at break remain practically the same.
  - Minor color changes and opacity: 10.0→13.9% (2 wt% talc).

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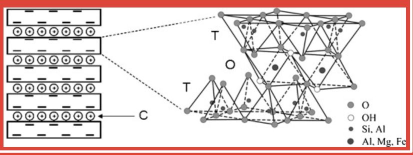
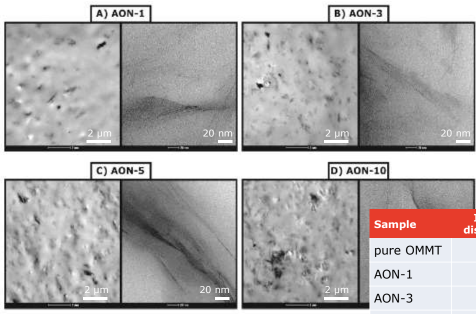
2. Effect of OMMT nanoclay in AON composites

- **Organomodified clay**
  - Layered silicate with very high aspect ratio
  - Montmorillonite modified with organic cationic surfactant octadecyl*bis*(2-hydroxyethyl)methylammonium chloride for better delamination and dispersion in polymer (= OMMT)
  - 0, 1, 3, 5 and 10 wt%



Distribution & dispersion of OMMT nanoparticles



Sample	Interlayer distance [nm]
pure OMMT	1.78
AON-1	3.76
AON-3	3.68
AON-5	3.63
AON-10	3.56

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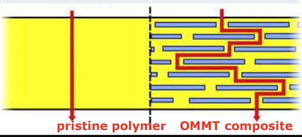
Vandewijngaarden J. et. al., **2016**, Effect of ultrafine talc on crystallization and end-use properties of poly(3-hydroxybutyrate-co-3-hydroxyhexanoate), *Journal of Applied Polymer Science*, 133(45).

Impact of OMMT on gas permeability

- **Gas permeability ↓↓ at higher OMMT content**
  - OMMT = physical barrier against gas diffusion

Sample	PO_2 [cm³.mm/m².day.atm]	PCO_2 [cm³.mm/m².day.atm]	$P_{water\ vapor}$ [g.mm/m².day]
AON-0	9.6 (± 0.8)	55 (± 2)	1.51 (± 0.06)
AON-1	8.7 (± 0.2)	51 (± 2)	1.41 (± 0.05)
AON-3	7.8 (± 0.5)	41 (± 2)	1.19 (± 0.02)
AON-5	7.3 (± 0.2)	39 (± 2)	1.0 (± 0.1)
AON-10	5.1 (± 0.3)	32 (± 1)	0.95 (± 0.07)



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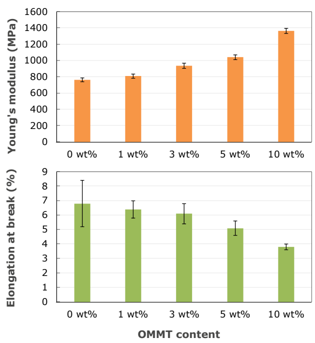
Impact of OMMT on tensile and other properties

- **OMMT-AON nanocomposites**
  - Stiffer
  - More brittle
- **Color**
  - slight darkening (ΔL)
  - slight ↑ in green (Δa)
  - outspoken yellowing (Δb)
- **Opacity**
  - 11.4% (AON-0)
  - 12.8% (AON-10)



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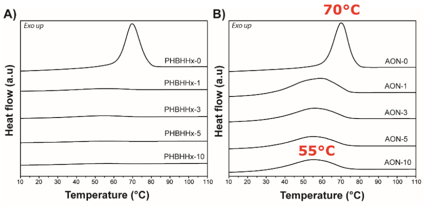
Retarded crystallization in presence of OMMT

- **OMMT**
  - OMMT works as a catalyst towards thermal degradation of the polymer, this is probably due to rapid moisture uptake by OMMT
  - During processing, moisture causes hydrolysis of polymer chains **→ slower crystallization**



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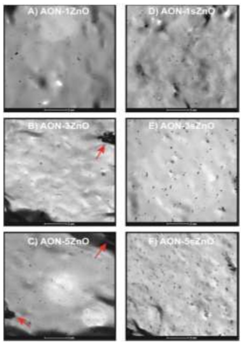
3. Effect of ZnO nanorods in AON composites

- **Zinc oxide (ZnO) is applied:**
  - to enhance vulcanization & thermal conductivity in rubber industry
  - as antibacterial, wound healing or nutritional additive, UV absorbent, etc. in pharmaceutical and cosmetic industry
  - as photocatalyst in treatment of organically polluted waste water
  - as filler in polymers
- **Zinc oxide**
  - can be synthesized in a great variety of nanostructures
  - surface modified for enhanced compatibility with polymer matrix

Dispersion in AON matrix

- **2 types of zinc oxide nanorods**
  - 1, 3 and 5 wt%.
  - unmodified (ZnO)
    - no fine dispersions
    - agglomerations
  - surface coated with triethoxy caprylylsilane (sZnO)
    - well-dispersed nanocomposites



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Vandewijngaarden J. et al., 2017, Modified Poly(3-hydroxybutyrate-co-3-hydroxy-hexanoate) with Interesting Properties for Food Packaging Applications, *proceedings 28th IAPRI symposium 2017*

Thermal stability & crystallization

- **ZnO**
  - has a slight catalytic effect on thermal degradation of the polymer, leading to a decrease in MW and thermal stability after processing.
- **sZnO**
  - partially counteracts thermal degradation due to deactivation of the zinc oxide surface by silanization.
- **Crystallization properties**
  - unmodified ZnO induces a decrease of 1.3°C in $T_{c,o}$ and 1.7°C $T_{c,p}$.
  - sZnO does not affect the crystallization properties of AON.

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Opacity of the sZnO/ANO nanocomposites

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Gas permeability of (s)Zn/AON nanocomposites

- **ZnO**: large impermeable clusters / visible voids and cracks (5 wt%)
- **sZnO**: no effect! Highly dispersible nanorods form very small clusters

Sample	PO_2 [cm³.mm/m².day.atm]	PCO_2 [cm³.mm/m².day.atm]	$P_{water\ vapor}$ [g.mm/m².day]
AON-0	9.0 (± 0.1)	42.9 (± 0.5)	1.37 (± 0.02)
AON-1ZnO	8.4 (± 0.2)	40 (± 1)	1.22 (± 0.03)
AON-3ZnO	8.6 (± 0.1)	40.0 (± 0.2)	1.22 (± 0.03)
AON-5ZnO	/	/	/
AON-1sZnO	9.0 (± 0.2)	43 (± 1)	1.38 (± 0.05)
AON-3sZnO	9.2 (± 0.1)	42.1 (± 0.3)	1.33 (± 0.03)
AON-5sZnO	9.2 (± 0.1)	42.9 (± 0.5)	1.30 (± 0.05)
AON-3TiO$_2$	9.0 (± 0.3)	42 (± 1)	1.35 (± 0.03)

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Tensile properties of (s)Zno/nanocomposites

- **ZnO** has similar effects as OMMT, although not as outspoken.
- **sZnO** renders AON stiffer, without losing too much of its ductility or tensile strength.

Sample	Young's modulus [Mpa]	Max. tensile strength [Mpa]	Nominal strain at max. load [%]	Nominal strain at break [%]
AON-0	704 (± 28)	19.1 (± 0.4)	5.8 (± 0.1)	7.4 (± 0.2)
AON-1ZnO	737 (± 23)	19.3 (± 0.3)	5.5 (± 0.2)	6.3 (± 0.1)
AON-3ZnO	792 (± 26)	18.8 (± 0.4)	4.8 (± 0.2)	5.7 (± 0.2)
AON-5ZnO	789 (± 29)	17.1 (± 1.0)	4.2 (± 0.4)	4.7 (± 0.2)
AON-1sZnO	719 (± 19)	19.0 (± 0.5)	5.9 (± 0.2)	6.9 (± 0.2)
AON-3sZnO	728 (± 25)	18.9 (± 0.7)	5.5 (± 0.2)	6.2 (± 0.2)
AON-5sZnO	751 (± 36)	18.8 (± 0.3)	5.4 (± 0.2)	6.0 (± 0.3)
AON-3TiO_2	770 (± 45)	18.8 (± 0.3)	5.4 (± 0.2)	6.2 (± 0.1)

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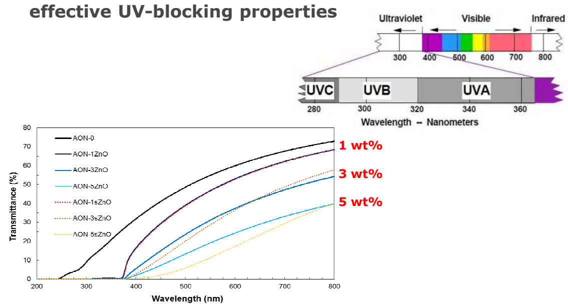
UV absorption properties

- **The (s)ZnO/AON nanocomposite films possess highly effective UV-blocking properties**



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Conclusion

- **PHBHHx shows potential for use as packaging material, but some drawbacks need to be faced**
  - Slow crystallization will hinder processing
  - Moderate gas barrier properties must be enhanced
- **Ultrafine talc**
  - Highly performant nucleating agent for PHBHHx
  - Reduced spherulite size and uniform distribution
  - At low concentrations, no significant effect on other investigated properties

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Conclusion

- **OMMT nanoclay**
  - Good compatibility between PHBHHx and OMMT
  - Gas permeability significantly reduced
  - PHBHHx rendered stiffer and more brittle at higher concentrations
  - Crystallization retarded → avoid moisture!
  - Additional orientation can be promising
- **sZnO nanorods**
  - ZnO surface modification yields excellent dispersion
  - Slight increase in stiffness/decrease in elongation at break
  - No reduction of gas permeability
  - UV-blocking = added functional property!

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Final conclusion

- This study showed that a single modification is not sufficient to achieve better packaging properties at the same time.
- Combination of additives and/or other modification techniques must be further investigated.

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Acknowledgments

- Thanks to prof. Philippe Dubois and dr. Marius Murariu for their continuous support in sample preparation and analysis and their helpful discussions during the PhD study of Jens Vandewijngaarden.
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