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ComBIOsites

Reversibly photocrosslinked BIO-based composites with barrier properties from industrial by-products

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Motivation

Packaging

39.9% of the total demand of 49 Mt of plastics in Europ... ...t)

Sustainability?

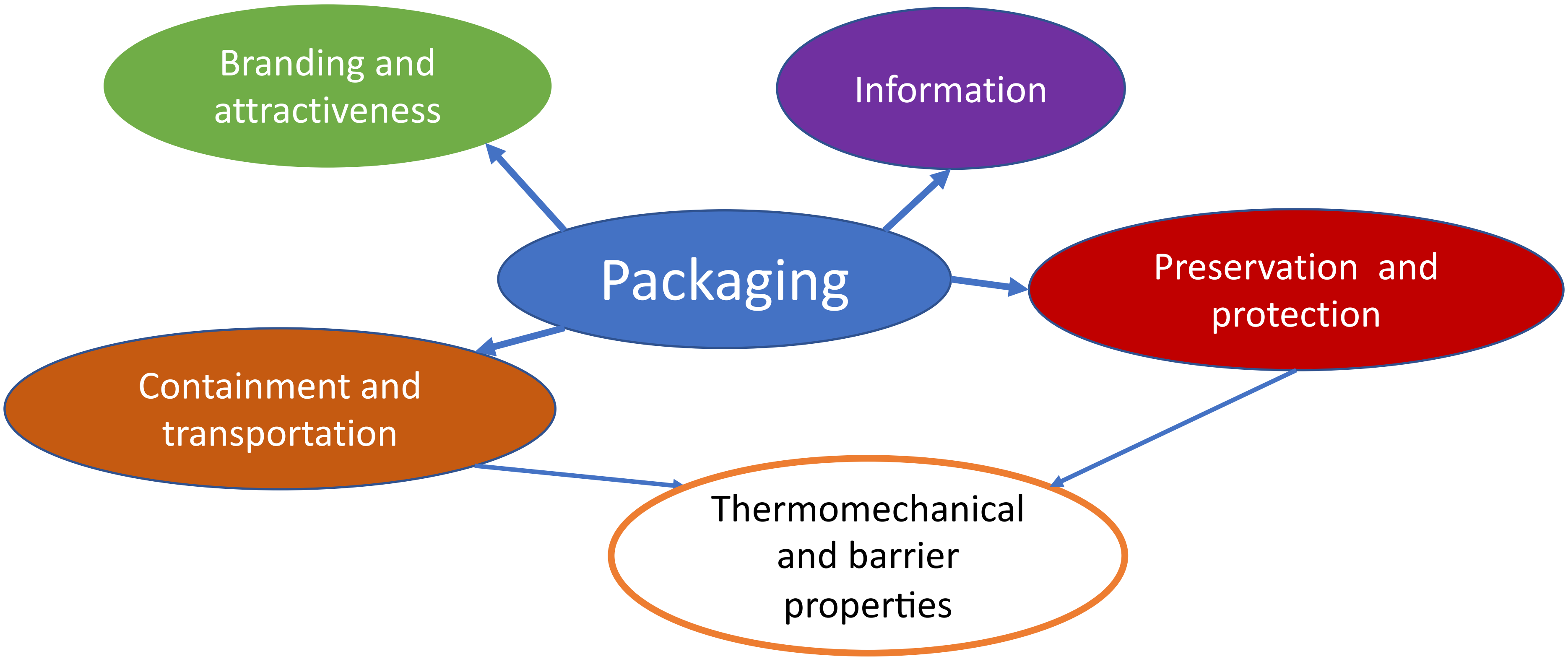
Plastic packaging recycling rate : 39.5% (7.7 Mt)

Waste reduction target (EC): recycling 55% of plastic packaging waste by 2025.

Reducing the environmental impact of packaging: bioplastics (bio-based and/or biodegradable)

Plastics the Facts 2016, PlasticsEurope www.plasticseurope.org (access: 20/08/2017)
Proposal for a Directive Of The European Parliament And Of The Council (COM/2015/0596 final - 2015/0276 (COD)).

Functions of packaging

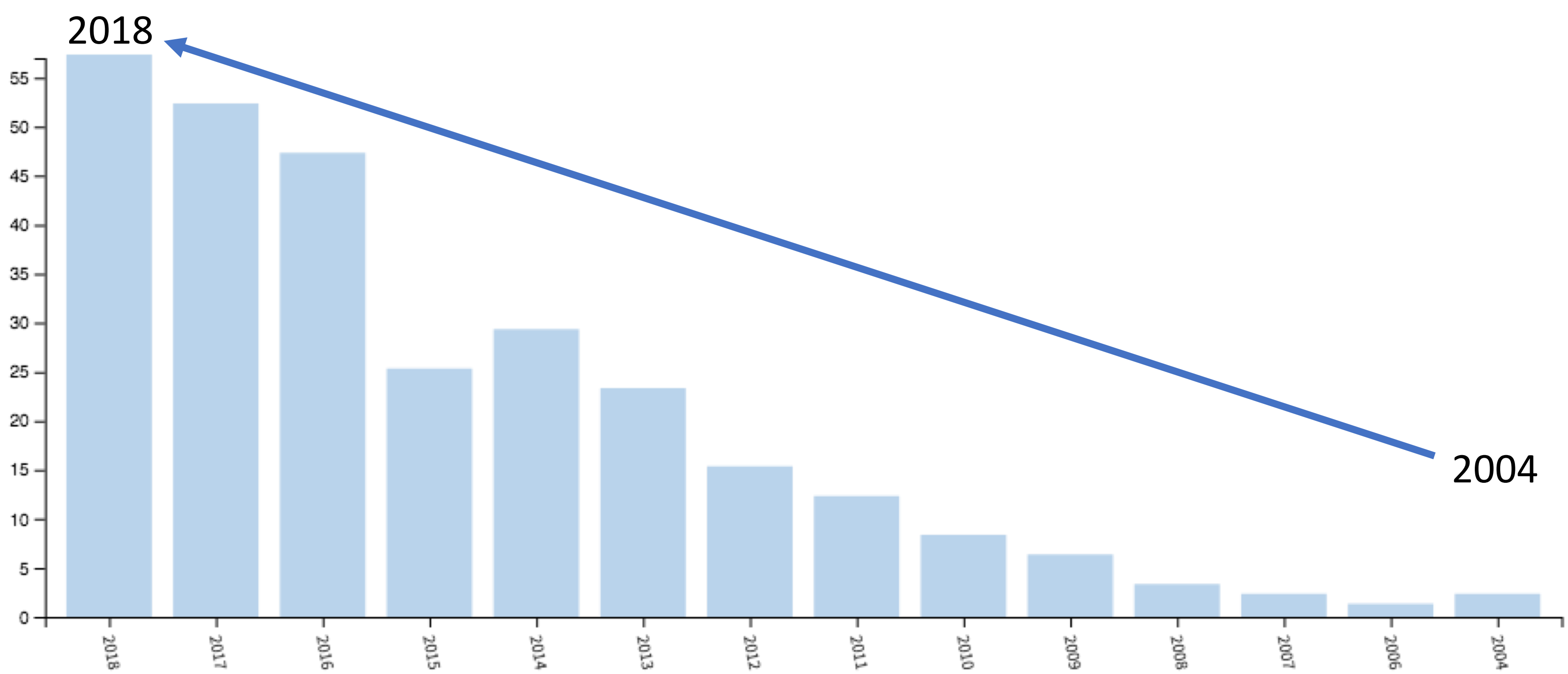


The challenge of a sustainable and recyclable barrier packaging material still needs to be addressed; petroleum-based plastic foils, or multilayer films that are not easily recyclable nor biodegradable, are mostly used

BIO-based barrier films

Web of knowledge search (# records per year):

TOPIC: ("bio-based" or biobased) *AND* **TOPIC:** (barrier or "low permeability") *AND* **TOPIC:** (film* or packag*)



BIO-based barrier films

23 März 2016

High barrier biobased flexible packaging: welcome Propylester Ingeo

The Metalvuoto metallized and coated film with excellent high barrier properties can be consi

Two companies
Metalvuoto an
Oxaqua® and I
solutions with
http://news.bi

Bio-based Barrier Film PLANTIC

2017 DuPont Award for Packaging Innovation Given for PLANTIC R

July 24, 2017
Plantic Technologies Limited
(The Kuraray Group)

PLANTIC R, produced by Plantic Technologies Limited (headquarters: Australia; President: Kenzo Okamoto), received the Diamond Finalist Award in the 2017 DuPont Award for Packaging Innovation (awarded by DuPont). PLANTIC R was recognized for its environmental friendliness and recyclability.

Overview of the Product and Reasons for the Award

- PLANTIC is a bio-based barrier film made mainly from a specialized form of starch. Because it is an effective oxygen barrier, it is used primarily in packaging materials for meats and fish. By helping to maintain food freshness, the product helps reduce food loss, contributing to both the food industry and environmental preservation.

- PLANTIC R, which received the Diamond Finalist a
film consisting of a barrier layer of bio-based PLAN
sheet laminated on both sides with polyethylene ter
(PET). The PET layers serve as barriers to water va
the PLANTIC HP layer serves as a barrier to oxyge
gases, helping preserve the freshness of fish and m
- Whereas typical multilayered films are difficult sepa
recycling, PLANTIC R can be recycled more easily,
solubility and biodegradability of the PLANTIC HP b
allow the PET to be recovered. The film is already b
recycled in Australia.

Bio-based multilayer transparent barrier films are now reality

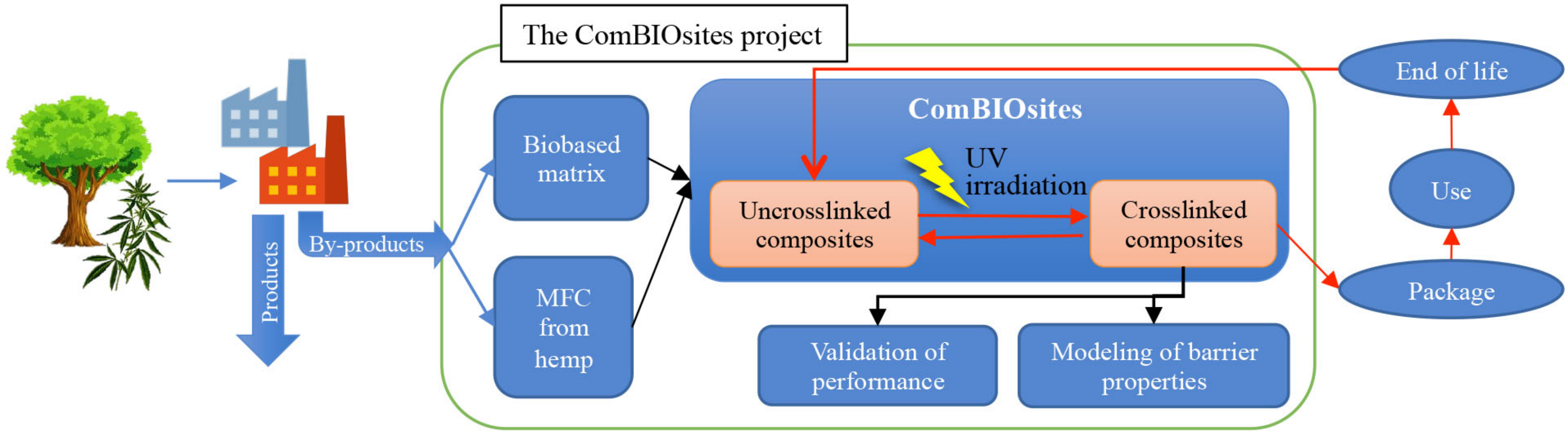
19.06.2018

Four key players in the bioplastics industry - Eurotech Extrusion Machinery, NatureWorks, Nippon Gohsei and Sukano - have successfully processed a multilayer transparent bio-based barrier film, offering a potential replacement for conventional fossil fuel-based structures in dry food packaging.

https://www.bioplasticsmagazine.com/en/news/meldungen/20180619Bio-based-multilayer-transparent-barrier-films-are-now-reality.

Our approach: ComBIOsites

Reversibly photocrosslinked BIO-based composites with barrier properties from industrial by-products



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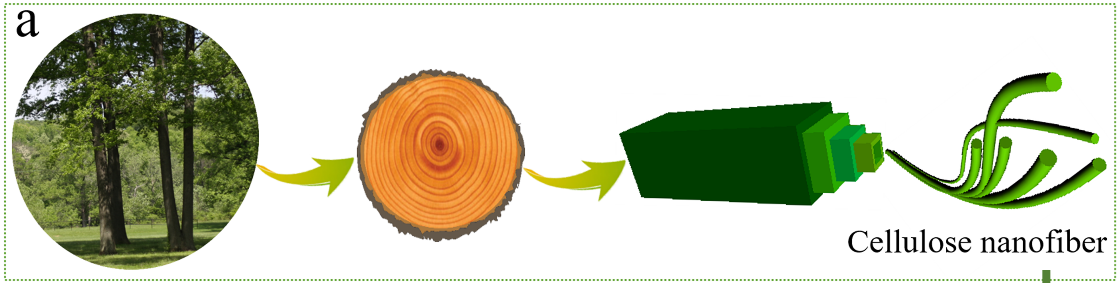
Microfibrillated Cellulose (MFC)

Cellulose: most abundant biopolymer on earth; renewable, sustainable, biodegradable.



Jiao L, et al. (2016) Natural Cellulose Nanofibers As Sustainable Enhancers in Construction Cement. PLoS ONE 11(12): e0168422.

Destructuration of cellulose sources: cellulose microfibrils (MFC), usually aqueous dispersions.

MFC films: good barrier against gases like O_2, CO_2 and N_2

Klemm, D., et al. Cellulose: Fascinating Biopolymer and Sustainable Raw Material. Angew Chem Int Ed. 44, 3358–3393 (2005)
García, A, et al. Industrial and crop wastes: A new source for nanocellulose biorefinery. Ind. Crops Prod. 93, 26–38 (2016).

MFC from by-products of Hemp decortication

- sustainable annual crop, low request of water and fertilizer, no need for agrochemicals
- able to improve soil structure
- suitable for the European climates

Primarily grown for:
- bast fibers (skin of the stem)
- seeds

By-product

about 70 w/w %

<u>Core of the stem:</u>

Higher value novel applications are being sought e.g. production of MFC and secondary bioethanol production

Carus, M. et al. T*he European Hemp Industry: Cultivation, processing and applications for fibres, shivs, seeds and flowers* (2016), European Industrial Hemp Association (EIHA), eiha.org/documents (30/08/2017)
González-García, et al, *Life cycle assessment of hemp hurds use in second generation ethanol production*. Biomass Bioenergy 36, 268–279 (2012).
Abraham, R et al. *Enrichment of Cellulosic Waste Hemp (Cannabis sativa) Hurd into Non-Toxic Microfibres*. Materials 9, 562 (2016).

Microfibrillated Cellulose (MFC): challenges

⚠ High hydrophilicity prevents use in highly humid environments ⚠

↓

Combine MFC with other (bio)polymers in the form of composites.

<u>water-soluble polymers:</u>

✓ processing in aqueous solution
✓ good filler dispersion
✗ poor water resistance.

<u>non water-soluble polymers</u>

✓ improved water resistance
✗ poor MFC dispersion
✗ complex processing

Processing in organic solvent:
✗ drying / solvent exchange
✗ agglomeration of MFC

Melt compounding:
✗ high T and shear
✗ fiber surface modification

Dufresne, A. Cellulose nanomaterial reinforced polymer nanocomposites. Curr Opin Colloid Interface Sci 29, 1–8 (2017)
Hubbe, M. A. et al. Nanocellulose in Thin Films, Coatings, and Plies for Packaging Applications: A Review. BioResources 12, 2143–2233 (2017)
Oksman, K. et al. Review of the recent developments in cellulose nanocomposite processing. Compos A Appl Sci Manuf 83, 2–18 (2016)

Photocrosslinking

✓ Green process, solvent-free and with low energy consumption (room T); fast polymerization process attractive for industrial use.

✓ Uncured prepolymers with very low viscosity: solvent-free mixing at room temperature

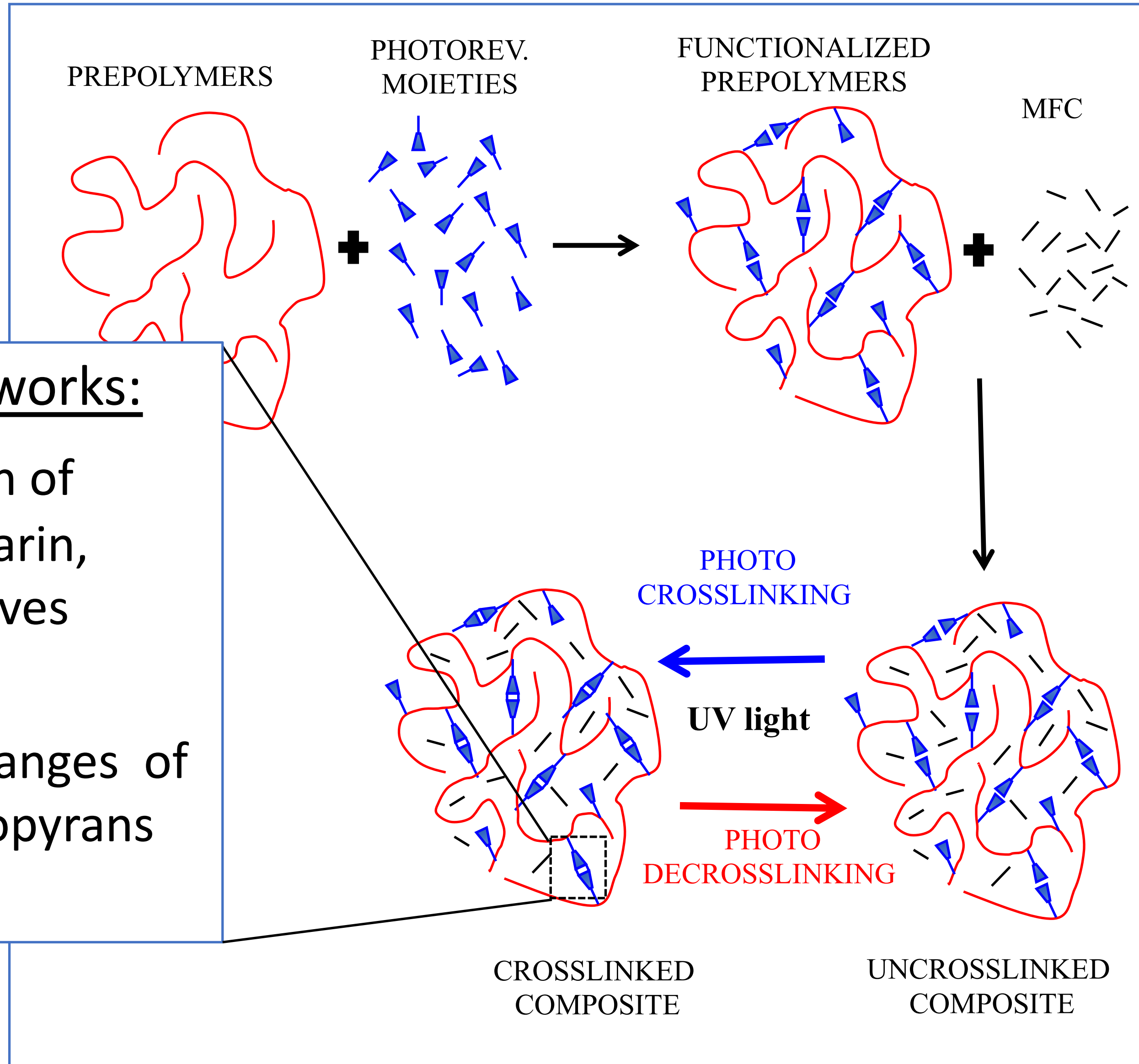
✓ insoluble cured material even for water-soluble prepolymers; high mechanical performances

✗ Crosslinking often hinders recyclability and biodegradability

- Obtain recyclable bio-based matrices by reversible photocrosslinking.
- Retain biodegradability of the biobased prepolymers
- Presence of natural fibers may accelerate biodegradation of crosslinked biopolymers in soil.

Silva, A. L. da et al. *Cardanol-based thermoset plastic reinforced by sponge gourd fibers (Luffa cylindrica).* Polímeros 26, 21–29 (2016)

Reversible photocrosslinking



Photoreversible networks:

- Photocycloaddition of anthracene, coumarin, cinnamoyl derivatives
- Photoinduced conformational changes of azobenzenes, spiropyrans

Jellali, R. et al Macromol. Biosci. 17, 1600495 (2017)
Tanchak O.M. et al, Macromolecules 2005, 38, 10566-10570
Tunc, D. et al. Macromolecules **47**, 8247–8254 (2014).

Project outline

WP1 **Synthesize reversibly photocrosslinked biopolymers:** chemically modify the pre-polymers with photoreversible groups, evaluate the extent and reversibility of photocrosslinking, assess the thermomechanical and the barrier properties of the crosslinked polymers, to validate the materials for use in the successive development of composites.

WP2 **Obtain MFC from hemp hurds**: preparation of MFC, based on known chemically assisted mechanical routes

WP3 **Produce reversibly photocrosslinked biopolymer/MFC composites** : define the process route for solvent-free mixing of MFC with the uncured functionalized prepolymers, at different concentrations; observe morphology and assess the effect of MFC on the reversible photocrosslinking reaction

WP4 **Determine process-property relationships for tailoring performance** : optimize the performance of the composites; thermal behaviour, mechanical properties, permeability to water vapour, O_2 and CO_2

WP5 **Phenomenological model for the permeability of the composite** : model the permeability of composites; investigate numerically the role of a number of variables, such as fibre aspect ratio and volume fraction of the disperse phase as well as the effects of fibre aggregation or preferential orientation in the matrix