



# LET'S CONNECT!

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and polymers sustainable development!

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## WG1

Synthetic approaches towards  
FDCA and related monomers

## WG2

Materials development, their processing and  
characterisation, and computational studies

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# WG1

**Synthetic approaches towards  
FDCA and related monomers**

WG1 is focused on the development of novel technologies for the synthesis of FDCA, among other furan monomers, starting from widely occurring non-edible alternative sources of starting sugars.

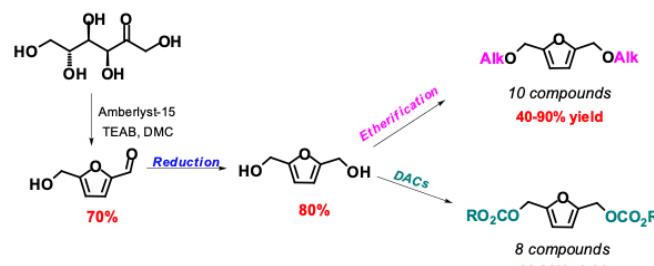


Figure 1. Synthesis of HMF from D-fructose and its conversions into BHMF and related monomers

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## Synthesis and derivatization of 2,5-bis(hydroxymethyl)furan (BHMF)

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Biomass-derived C6-furanic platform chemicals are regarded as the most promising building blocks in biorefinery exploitation. 5-Hydroxymethylfurfural (HMF) is referred as a “sleeping giant” in consideration of its potential in bridging the gap from a fossil-based chemistry to a more sustainable one. HMF is a versatile substrate with enormous market potential as it can be easily converted into high value chemicals, materials and bio-based polymers.[1] However, there are some limitations in developing an efficient HMF-based chemistry, i.e., its preferred solubility in water rather than in organic solvents, the absence of a cost-efficient scale-up synthesis, and well known HMF stability issue partially solved by the addition of small amount of specific stabilizers.

In our laboratory we have developed a new approach to HMF from D-Fructose using dimethyl carbonate as an extracting solvent in the presence of an acidic heterogenous catalyst. This synthesis is easily scalable up to 20 grams of D-fructose and allows to recover HMF in 70% isolated yield.[2] Quick reduction of HMF to the related 2,5-bis(hydroxymethyl)furan (BHMF) was

also carried out using sodium borohydride as reducing agent. This latter approach led to prepare rapidly a rather large amount of BHMF. As a result, BHMF derivatization was also investigated. In particular we have focused on BHMF etherification reaction to achieve 2,5-bis(alkoxymethyl) furans (BAMFs) – well-known biofuel candidates. Several catalysts were investigated; (mild) reaction conditions were optimized and thus employed for the preparation of a library of BAMFs (10 compounds). Products isolation and purification were addressed for each BAMFs.[3] Two examples of etherification reactions were also conducted in gram-scale i.e. for the synthesis of 2,5-bis(methoxymethyl)furan and 2,5-bis(isopropoxymethyl) furan.

Ongoing research on BHMF includes studying its reactivity with dialkyl carbonates. The idea is to develop a library of easy accessible bio-based monomers for polycarbonate, polyurethanes as well as potentially interesting intermediates for surfactants and detergents production.[4]

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## Synthesis and Characterization of Novel Vanillin-based Polyesters



Biomass-derived C6-furanic platform chemicals are regarded in recent years, fuelled by environmental concerns combined with economic issues, the scientific community is striving to find more sustainable products and processes. The valorisation of biomass is a key step in the quest for greener polymers.<sup>[1]</sup> In this context, lignin valorisation has attracted a lot of interest. Lignin is the second most abundant natural polymer and the richest renewable source of aromatic monomers. For the time being, vanillin is the only commercially available lignin-derived monomer<sup>[2]</sup> and is thus garnering a constantly increasing attention as a starting monomer for the preparation of bio-based thermoplastic and thermoset polymers.<sup>[3]</sup> Herein, we will present the work of our research group on vanillin-based polyesters.

[4] Vanillic acid has been derivatised via a Williamson reaction to yield  $\omega$ -hydroxyalkylene vanillic acids which were further polymerized to afford aliphatic polyesters bearing ether bonds. Poly(ethylene vanillate) has demonstrated similar thermal properties to PET. Copolymers with ethylene furanoate were also prepared. Indeed, poly(ethylene furanoate) (PEF) is the most prominent member of the family of furandicarboxylate polyesters and is considered the renewable substitute of poly(ethylene terephthalate) (PET), with the first commercial products expected for 2023, therefore furanoate/vanillic copolymers are very interesting to investigate. We will present the synthesis, structural characterization, thermal properties and crystallization behaviour of these promising polymers.



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## Pretreatment/fractionation and conversion of lignocellulosic biomass towards enhanced furanics production

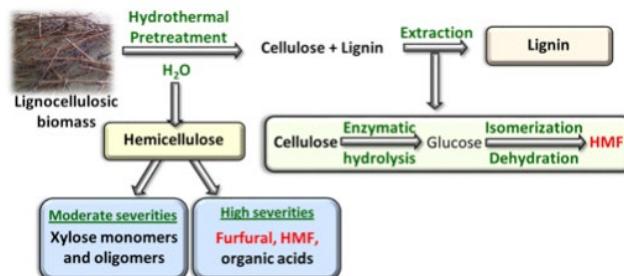


Figure 1. Scheme of lignocellulosic biomass hydrothermal pretreatment towards furanics production.

Lignocellulosic biomass derived from non-edible crops, agricultural and forestry residues as well as food industry wastes could be an alternative source of fuels and value-added chemicals. Within a “biorefinery” context, a “whole biomass” valorization approach is described in this work, as outlined in Figure 1. The first and more essential step is the pretreatment of biomass aiming to the fractionation into its main structural components: cellulose, hemicellulose and lignin. The fractionation could be achieved via the hydrothermal treatment in pure water, a “green” process with a lot of advantages, among them the limited use of organic solvents and catalysts, the variety of the applied feedstocks and the control of fractions composition through the selection of operational conditions (temperature and time).

The hydrothermal pretreatment results in the hemicellulose removal in liquid fraction and a cellulose-lignin solid [1-2]. At low and moderate severities, the liquid fraction is rich in xylose monomers/oligomers with hemicellulose recovery ~60% while under high severities, complete removal of hemicellulose is achieved and conversion of xylose is enhanced towards furanics

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# WG1

Synthetic approaches towards  
FDCA and related monomers

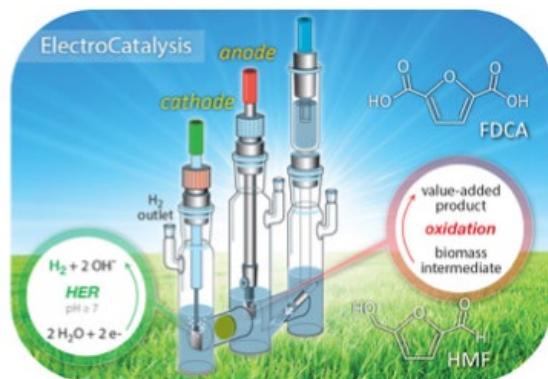
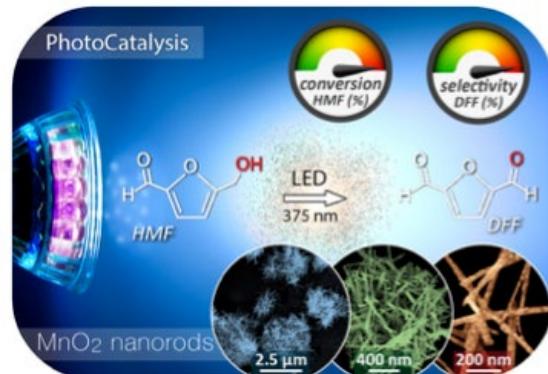


Figure 1. Manganese(IV) oxide nanorods for additive-free photo-assisted selective partial oxidation of HMF to DFF under ambient conditions (a) and a simplified schematic illustration of a prototype electrochemical cell (electrolyzer) for the simultaneous formation of H<sub>2</sub> and oxidation of biomass-derived compounds (b).

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## Photo- and electro-catalytic oxidation of 5-hydroxymethylfurfural to 2,5-diformylfuran or 2,5-furandicarboxylic acid



The sustainable production of valuable building blocks and polymers derived from natural and renewable resources still remains a global research and technological challenge.[1-2] 5-hydroxymethylfurfural (HMF) is one important platform chemical that can be obtained from lignocellulosic biomass and can be utilized as a feedstock in order to obtain two valuable building blocks: 2,5-diformylfuran (DFF) and 2,5-furandicarboxylic acid (FDCA). Photocatalytic oxidation (PCO) and electrochemical oxidation (ECO) are emerged as promising sustainable alternatives to more classical chemo-catalytic processes. Additionally, the simultaneous production of H<sub>2</sub> at the cathode in ECO systems can be an asset that elevate the green character of ECO. Going a step further, photoelectrochemical (PEC) catalysis also attracts the last

years the research attention, in order to eliminate the application of external bias by utilizing sunlight as a source of power. Towards efficient HMF upgrade by PCO, ECO or PEC methods, the rational design of efficient nano-engineered catalysts is the key aspect. Herein, we present our recent developments on the design and application of manganese (IV) oxide nanorods for the additive-free photo-assisted selective partial oxidation of HMF to DFF under ambient conditions (>99% HMF conversion and 100% DFF selectivity).[3] Moreover, we present the recent trends related to the nanoengineered anodes for ECO and PEC applications for the oxidation of HMF to FDCA, with an emphasis on the crucial structural, morphological and chemical features of the nanostructured materials used as anodes.



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## Development of molecular catalysts for transformation of bio-derived furans

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The development of new catalysts for the transformation of biomass derived compounds into valued-added chemicals and liquid fuels is highly desirable to overcome the key challenges for market penetration of sustainable biomass-based products. We are currently modeling two processes involving bio-derived furans: 1) conversion of 5-hydroxymethylfurfural (HMF) to 2,5-furandicarboxaldehyde (DFF), and 2) Transformation of furoic acid (FA) into 2,5-furandicarboxylic acid (FDCA).

HMF is one of the most promising biomass-based chemicals that has the potential to be converted to a variety of useful intermediates for polymers and many other fine chemicals. DFF is a versatile precursor in the synthesis of functional polymers,

pharmaceuticals, antifungal agents, and furan-urea resins.[1] FDCA is one of the most important “platform molecules” due to its potential application as a monomer in the synthesis of green polymers.[2]

In this communication we report our advances in development efficient complexes to catalyse the transformation of HMF to HMF by an electrochemical procedure, and the transformation of FA to FDCA by homogeneous catalysis. The metal complexes employed metal ions (manganese, cobalt, and zinc) in the +2 or +3 oxidation state, and two families of organic ligands: i) imine-imine Schiff bases (Figure 1), and ii) Mannich bases type derivatives.

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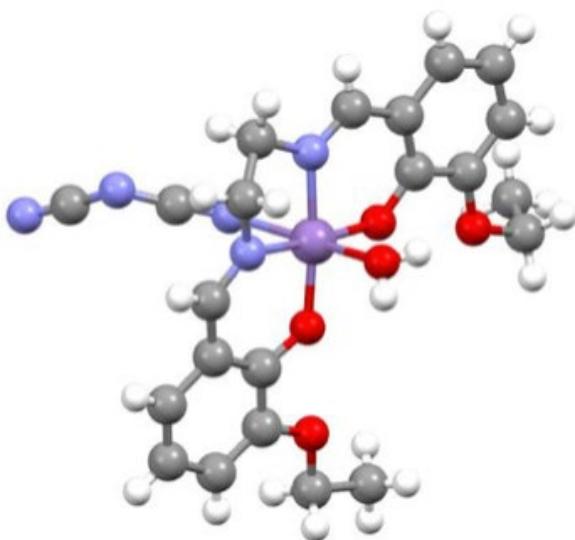


Figure 1. Crystal structure of the [Mn(III)(6,6'-(ethane-1,2-diylbis(azaneylylidene))bis(methaneylylidene))bis(2-ethoxyphenolate)(dicyanamide)(aqua)], an efficient catalyst for electrochemical conversion of HMF to DFF.

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## WG2

**Materials development, their processing and characterisation, and computational studies**

WG2 is focused on the synthesis of novel furan-based polycondensates using FDCA or derivatives and other renewable-based monomers. Emphasis is made on their green synthesis, concomitantly with their technical feasibility.

A second scientific focus of WG2 is the preparation of (nano)composites and hybrid materials from selected furan polymers and bio-based elements.

Materials processing and detailed characterisation applying both routinely used procedures (mainly structural, thermal and mechanical techniques, but also barrier and biodegradation); as well as, highly specialised ones are being carried out.

# WG2

Materials development, their processing and characterisation, and computational studies



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## Shape memory behavior of fully bio-based Aromatic-aliphatic copolymers

“

Over the last decade, development of bio based polymers has become one of the principal focuses of research in materials science, which is related to environmental awareness over gradual exhaustion of non-renewable resources. 2,5-furandicarboxylic acid (FDCA) stands out as a highly potential bio-based monomer able to replace petro-derived terephthalic acid.[1] FDCA and its derivatives can be used, among others, to obtain copolymers with interesting properties, such as shape memory effect. Shape-memory polymers as stimuli-responsive shape-changing polymers are of great interest for fundamental research and technological innovation. It is known that shape memory materials display the ability of changing their shape in response to external stimuli, such as changes in temperature.[2]

In the present study, the mechanical and thermal properties of novel 100% bio based random copolymers were investigated. The poly(trimethylene 2,5-furanoate-co-trimethylene sebacate) copolymers (PTF-co-PTSeb) and poly(trimethylene 2,5-furanoate-co trimethylene suberate) copolymers (PTF-co-PTSub) containing from 5 to 25 mol % of trimethylene sebacate units (TSeb), or trimethylene suberate units (TSub) were synthesized by a two-stage melt polycondensation process using dimethyl esters of 2,5-furandicarboxylic acid (DMFDCA), bio-1,3-propanediol (1,3-PD) and dimethyl sebacate (DMSeb) or dimethyl suberate (DMSub), depending on the copolymer. The obtained copolymers were studied concerning their thermal properties and mechanical performance. Additionally, the thermally induced shape memory effect was investigated, using DMTA analysis. The values of shape fixity and shape recovery were determined.

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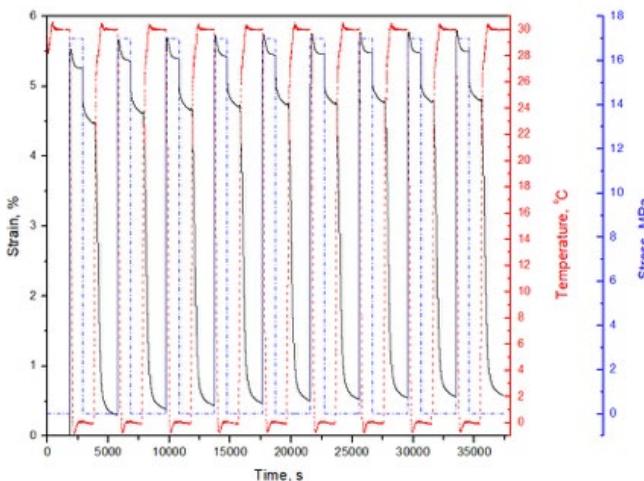


Figure 1. Shape memory cycles of PTF-co-25PTSub copolymer.

The studies were partially financed by the National Science Centre within project SONATA no 2018/31/D/ST8/00792.  
This abstract is based upon work from WG2.

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# WG2

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Figure 1. Poly(2,5-furandicarboxylate)s 1

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## Overview on poly(2,5-furandicarboxylate)s made in University of Aveiro

“

There is today a global challenge for sustainability, in particular polymers' development are also deeply engaged with this challenge. Therefore, in the past decade at the University of Aveiro, we have been dedicated to the research and development of poly(2,5-furandicarboxylate)s, as alternative polymers from biomass 1.

The initial focus was on the synthesis and characterisation of poly(ethylene 2,5-furandicarboxylate) (PEF), the so-called renewable counterpart of poly(ethylene terephthalate) (PET) 2,3. Afterward, we introduce a new leitmotif in the furan polymers development – the (bio)degradable furanic-aliphatic copolymers, for instance the copolymers based on PEF and PLA 4.

Then, we extended the concept to homopolymers with poly(1,20-eicosanediyl 2,5-furandicarboxylate) 5 which has interest among food packaging applications (equilibrium moisture uptake very near 0% due to its hydrophobic character but biodegraded). More recently, our focus turned also to use tailor degradation in recycling.

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# WG2

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Figure 1. Utilization of kraft (nano)lignin as epoxy polymer additive.

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The research work was supported by the Hellenic Foundation for Research and Innovation (HFR) under the HFRI PhD Fellowship grant (Fellowship Number: 967)

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## Kraft (nano)lignin as epoxy polymer additive

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Lignin is one of the three main structural components of lignocellulosic biomass, representing the most abundant natural source of aromatics and phenolics. Lignosulfonates, Kraft lignin and related types of lignins that are recovered in huge amounts as side products in the pulp and paper industry, are currently highly underutilized as they have been traditionally used for the in-house production of heat and energy [1]. In the last decades, due to its highly aromatic/phenolic nature and hydroxylated surface, lignin has attracted a lot of scientific and industrial interest, especially in the polymer science field, aiming towards its utilization either with or without functionalization towards the production of new green-based polymers and composites [2].

In this work, Kraft lignin was utilized towards the production of lignin-based epoxy composites, as presented in Figure 1. Kraft lignin was used either as received or after chemical or mechanical treatment/fractionation that included solvent fractionation, glycidylation and ball milling. The fractionation of kraft lignin in ethanol resulted in separation of nano-lignin while its functionalization with epoxy rings (glycidylation) was achieved via reaction with epichlorohydrin in a methanolic sodium hydroxide solution at 80°C. Ball milling was performed with 8-agate balls for

2 and 8 h. Structural and morphological characteristics of initial and treated lignins were investigated using SEM, FT-IR, GPC, NMR, TGA etc.

Initial kraft lignin was tested as a curing agent and as a filler/additive in the lignin/epoxy composite using commercially available epoxy resin, i.e. diglycidyl ether of bisphenol A (DGEBA) and Jeffamines D-230 (glassy system) and D-2000 (rubbery system) as curing agents when needed. Treated kraft lignins were also studied as additives in the epoxy composites. The composites were prepared by in-situ polymerization, followed by curing at selected conditions. The mechanical properties of the prepared composites were tested using tensile measurements. The glassy epoxy composites containing initial kraft lignin and all treated lignins (nano-, ball milled- and glycidylized lignins) exhibited increased strength and stiffness at low loadings (3 wt.%) and gradual deterioration of mechanical properties at higher loadings. In the rubbery lignin/epoxy composites containing initial and treated kraft lignins, a substantial increase in the mechanical properties was achieved at low lignin loadings (3 wt.%), while increase of lignin loading resulted in further improvement in strength, elongation and stiffness.

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# WG2

Materials development, their processing and characterisation, and computational studies



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## Tuning the properties of furan-based polyesters via the in-situ incorporation of nanofillers

“

Chemicals from vegetable feedstocks have been proposed as monomers for polymer production. Sugars available within the biorefinery can be converted to a family of products, including dehydrosugars, furans, and levulinic acid by dehydration. 2,5-furandicarboxylic acid (2,5-FDCA) is an important member of the furan family that can be formed by an oxidative dehydration of glucose. It has a large potential as a replacement for terephthalic acid, a widely used component in various polyesters. Furan based polyesters have been reported for years and recently furan-based nanocomposites are getting attraction. Polymer nanocomposites based on graphene, carbon nanotubes (CNTs), and layered silicates have been prepared to improve the mechanical, thermal, electrical, and gas barrier properties of neat polymers.

In nanocomposites dramatic changes in properties are possible at very low filler loadings (< 2 vol%). This depends on the inherent properties of the nanofiller, but also on the dispersion, interface chemistry and nanoscale morphology, which takes advantage of the enormous surface area per unit volume of nanofillers. In the in-situ polymerization method, the nanoinclusions are dispersed in the monomer and polymerization follows. A higher amount of fillers may be effectively dispersed with this method. Strong interactions with the polymer are also formed. In this work, polymer nanocomposites with various fillers based on poly(propylene furanoate) have been in-situ synthesized and were investigated with respect to their crystallization and melting behavior along with their mechanical properties.

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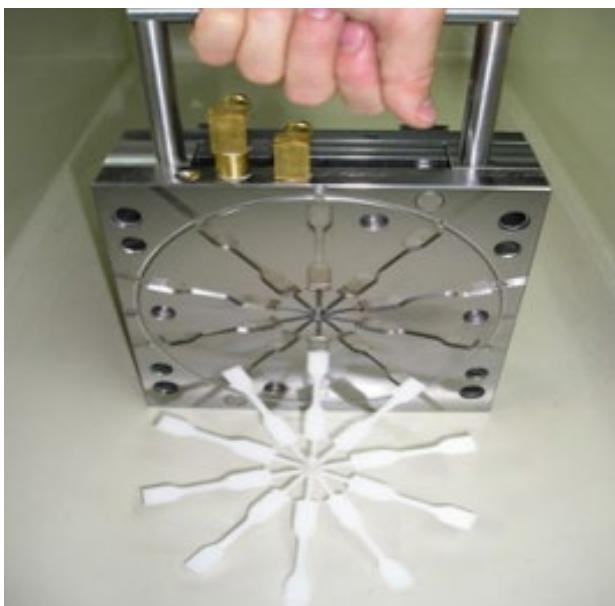


Figure 1. The injection molded samples for further characterization.

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## Activity in furan – based polyester copolymers at wput: materials synthesis and characterization

“

Our research are focused on the synthesis and characterization of furan – ester multiblock copolymers containing different types of flexible segments, possibly also bio-based. The main idea is to develop a new group of polymer materials with the features of thermoplastic elastomers, but more sustainable and environmental friendly. Combining different furan-ester segments with different diols we are trying to recognize and understand the interactions between the chemical structure, resulting supermolecular structure (as an effect of furan ring specific architecture), and materials performance, particularly their mechanical and elastic behaviour. We are able to synthesize the copolymers with different rigid to flexible segment ratio via polycondensation in melt with the output of 120 – 150 g as well as to prepare (dog-

bone) samples via injection molding (Fig. 1) or thin films in compression process. In our studies we have already investigated the copolymers based on poly(trimethylene furanoate) (PTF), poly(butylene furanoate) (PBF), poly(ethylene furanoate) (PEF) or poly(neopentylene furanoate) (PNPF) as rigid segments and fatty acid dimer diol (FADD), bio-based poly(tetramethylene ether) (PTMG) or poly(ethylene glycol) (PEG) as flexible segments [1-5]. The materials combine a wide range of physical properties, also the elastomeric behavior, with processability and good thermal stability, however an evident effect of the furan ring of material's crystallizability, thus specific multiphase structure, is observed. We offer our materials for further investigations of their structure and physical properties.

”

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## Nanocomposites based on poly(alkylene furanoate) *in situ* reinforced by various nanofillers: Crystallization and dynamics

“

Polymers and polymer nanocomposites have found extensive use in our everyday life and the industry, as they demonstrate tremendously improved properties when comparing with neat polymers and conventional composites. Recently, our world faces serious environmental challenges, including the use of commodity plastics, the latter being prepared from finite resources and exhibiting non eco-friendly character, such as slow biodegradability, hazardous recycling routes etc. The development of biodegradable polymers during the last decade has become the main solution. The biobased polyesters synthesized from 2,5-furan-dicarboxylic acid[1], a renewable building block derived from 5-hydroxymethylfurfural sources, known as poly(alkylene 2,5 furandicarboxylate)s, form a novel class of materials targeted to replace their fossil-based homologues quite soon. The said polyesters have already found use within packaging applications, owing to their excellent gas barrier properties and good mechanical performance. The latter is strongly connected with the crystalline fraction, CF, thus, crystallizability is the key factor for tuning the materials performance.

In our recent works[2-6], we have demonstrated the potential for tuning the crystallizability of three furan based polyesters, namely, poly(propylene-butylene- hexylene- furanoate)s (PPF- PBF- PHF-), by reinforcing the polymer via the *in situ* introduction to the matrix of low amounts of various nanofillers. These consist of carbon nanotubes, graphene, graphene oxide, montmorillonite clays and halloysite nanotubes. The reinforcing agents differ in the shape-geometry, surface area, aspect ratio and surface chemistry (modifications). The complementary techniques being employed for the nanocomposites characterization are: calorimetry, X-rays, microscopy, nanoindentation, IR and dielectric spectroscopy.

All unmodified fillers were found to offer additional crystallization sites, thus, to accelerate crystallization and mainly increase CF. This improvement was demonstrated to correlate with the initial specific surface area of the fillers. The results suggest also alternations in the semi-crystalline morphology, i.e. on the size, number and distribution of the formed crystals. Thus, both direct and indirect effects of the fillers were recorded, however systematic, on the mechanical performance, e.g. by increasing the elastic modulus. The implementation of increased interfacial interaction, achieved via surface modifications of the fillers resulted in opposite effects on crystallization (slower), which is shown here for the first time.

From the basic physics point of view and regarding molecular dynamics, the glass transition (calorimetry) and segmental dynamics (assessed by dielectric spectroscopy) were found to change indirectly with the filler presence, i.e. via changes in the crystallization and/or the drop in the molecular weight (due to the *in situ* synthesis). Interestingly, the local polymer dynamics was found to be sensitive to the early stages of crystallization, whereas in some nanocomposites additional dynamics processes were recorded, most probably arising from the polymer dynamics in the vicinity of the particles.

Overall, we have demonstrated that these systems provide high possibilities for tailor-making systems, also envisaging their employment in a wide range of applications.



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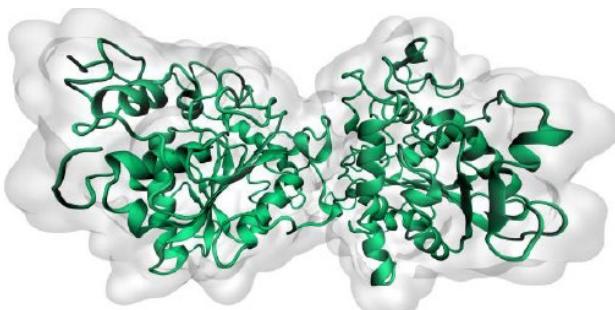


Figure 1. Description of CalB structure.

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## QM/MM molecular dynamics of PCL enzymatic synthesis

“

Bio-based polymers have attracted much attention in the biomedical field, especially in tissue engineering[1] but also as drug-delivery systems,[2] since these materials are non-toxic, bio-degradable bio-resorbable and bio-compatible.[3] Poly( $\epsilon$ -caprolactone) is one of these bio-based polymers, that its slow degradation rate has been exploited for several biomedical applications, such as tissue engineering, surgical sutures, drug-delivery systems, and scaffold fabrication technologies.[4]

Enzymes, particularly lipases, can be employed in the synthesis of these materials. They are hydrolases for the carbonyl ester bond of hydrophobic substrates, namely triacylglycerols, phospholipids and other insoluble substrates, acting in aqueous reacting medium,[5] as well as, in organic solvents (conditions with high interest for industrial applications).[6]

In this work we investigated the full catalytic cycle of *Candida antarctica* lipase B (CalB) for the ring-opening polymerization (ROP) of  $\epsilon$ -caprolactone in toluene,[7] using Quantum Mechanical/Molecular Mechanical Molecular Dynamics (QM/MM MD) calculations.[8]

”

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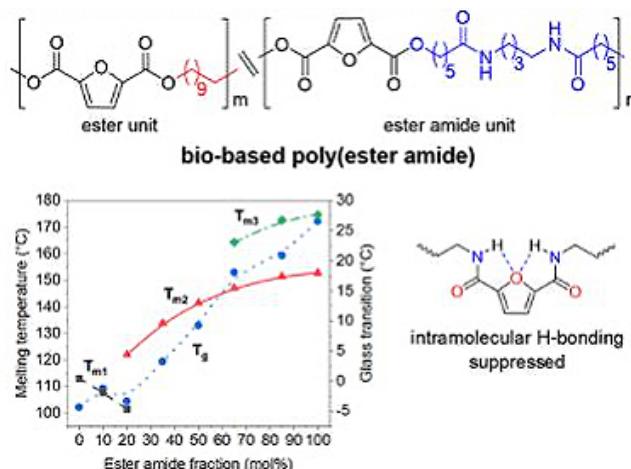


Figure 1. Thermal properties of the biobased poly(ester amides)

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## A facile method to synthesize semicrystalline poly(ester amide)s from 2,5-furandicarboxylic acid, 1,10-decanediol, and crystallizable amido diols

“

The synthesis of polyamides and poly(ester amide)s derived from 2,5-furandicarboxylic acid frequently leads to amorphous polymeric materials. Formation of intramolecular hydrogen bonds between the oxygen heteroatom in the furan ring and hydrogens of the amide bonds reduces the intermolecular hydrogen bonds that are usually responsible for the high thermal and mechanical performance of these materials. [1,2] To circumvent this problem, we recently reported the synthesis of aliphatic–aromatic poly(ester amide)s dimethyl 2,5-furandicarboxylate, 1,10-decanediol, and a preformed aliphatic diol containing two internal amide bonds (amido diol). Wide-angle X-ray diffraction and differential scanning calorimetry experiments revealed that polymers obtained were semicrystalline over the whole composition range and crystallized rapidly from the molten state, indicating that intramolecular H-bonding

is effectively suppressed. Depending on the ratio of 1,10-decanediol and amido diol, the thermal properties could be adjusted over a wide temperature range. The polymers exhibit  $T_g$  and  $T_m$  in a range of –4 to 27 °C and 102 to 175 °C, respectively. Elastic modulus and hardness increased almost linearly with the amount of ester–amide moieties. The method presented herein allows for the successful synthesis of semicrystalline poly(ester amide)s from 2,5-furandicarboxylic acid without undesired intramolecular hydrogen bonds. This finding could set the stage for further bio-based poly(ester amide)s from 2,5-furandicarboxylic acid suitable for high-performance applications.

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## Towards novel lignin-based aromatic polyesters: Synthesis and thermal behavior of poly(propylene vanillate)

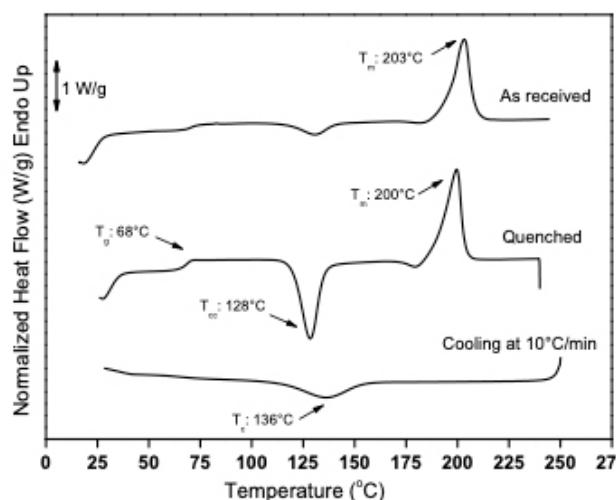


Figure 1.DSC scans of poly(propylene vanillate).

In recent years, the depleting stocks of fossil fuels combined with the growing environmental concerns over the excessive emissions of greenhouse gases and the accumulation of synthetic plastics in terrestrial and aqueous recipients, contribute to the flourishing interest both from academia and industry in the production of novel bio-based polymeric materials.[1] In this context, lignin, the second most abundant natural polymer, can be promoted for the synthesis of biomass-based monomers and the preparation of greener polymers, reinforcing the circular economy. Vanillic acid (VA) or 4-hydroxy-3-methoxybenzoic acid, that can be derived from lignin, is among the aromatic compounds that have been studied as potential candidates to produce fully or partially biobased polymeric materials with aromatic moieties, including polyesters.[2] Herein, the synthesis, thermal properties and crystallization behavior of poly(propylene vanillate) (PPV), an aliphatic biobased polyester, produced from 4-(2-hydroxypropoxy)-3-methoxybenzoic

acid, are reported. Since phase transitions strongly influence the processing of polymers and determine its temperature window, the melting, crystallization and glass transition temperatures of PPV have been measured, and the thermodynamics and kinetics of phase changes have been studied. The enthalpy of fusion has been estimated and the equilibrium melting temperature has been calculated via Hoffmann-Weeks method. The multiple melting behavior of PPV has been interpreted based on the melting-recrystallization model, while the isothermal crystallization has subsequently been studied. Finally, since processing is always dynamic in industry, the non-isothermal crystallization profiles from the melt or from the glass that have been investigated, using several techniques, such as differential scanning calorimetry (DSC), wide-angle X-ray diffraction (WAXD) and polarized light microscopy (PLM), will be presented.

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## 2,5-furanedicarboxylic acid as a building block for functional metal-organic architectures

“

Within the broad field of Chemistry of Polymers, Coordination Polymers (CPs) represent a class of metal-organic architectures composed of metal nodes and ligands arranged into a polymer structure extending in one, two, or three dimensions.[1] Metal-Organic Frameworks (MOFs) are an important subclass of porous coordination polymers which possess a high diversity of structural types and find extraordinary applications in many different branches of modern chemistry and materials science, including gas storage, selective sorption and sensing, catalysis, luminescence, and biomedical fields. An extremely high current interest in CPs and MOFs can be explained by their unique structural characteristics (crystallinity, porosity, huge surface area, stability, well-defined structures, etc.) and diverse functional properties.

For example, Wilmer, Hernandez, and Farha recently defined “MOFs as The Plastics of the 21st Century” and highlighted their current and future significant role in everyday life, following the evolution of organic polymers in the 20th century.[2]

In pursuit of our general research on the design and application of new functional CPs and MOFs driven by carboxylate building blocks,[3] this contribution highlights our recently initiated research lines toward exploring 2,5-furanedicarboxylic acid (FDCA) as a versatile bio-based linker for synthesis of metal-organic architectures and derived materials. These research lines include:

1) FDCA & Coordination Chemistry: Use of FDCA as a bio-based building block with five potential coordination sites for the self-assembly synthesis of new coordination compounds with Cu, Ag, Zn, and other metals, including metal complexes, coordination polymers or metal-organic frameworks.

2) FDCA & Catalysis: Application of the obtained coordination compounds as catalysts for the mild oxidative functionalization of various organic substrates, including precursors of FDCA (e.g., Cu-catalyzed oxidation of 5-hydroxymethylfurfural (HMF) to 2,5-furanedicarboxylic acid). Application of FDCA as an acid co-catalyst in oxidation of hydrocarbons.

3) FDCA & Antimicrobial Materials: Application of the obtained MOFs as antibacterial and antbiofilm materials, including the use of organic FDCA-based polymers as matrices to support diverse bioactive (bactericidal) molecules.

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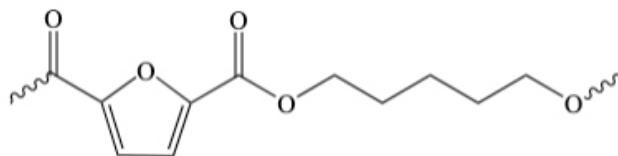


Figure 1. Chemical structure of Poly(pentamethylene furanoate) PPeF.

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## Structure, dynamics and barrier performance relationship in poly(pentamethylene furanoate)

“

Plastic waste has become a matter of great concern in recent years and is pushing governments and society to find new strategies to face the problem. Indeed, plastics cover up about 50% of primary food packaging, thanks to their low price, lightness, easy production and processability, modulation of properties and durability. Even though since 2006, the amount of plastic waste recycled has doubled, however a large amount of waste is still disposed in landfill[1] or, even worse, in the environment. In order to reduce environmental impact, the use of bioplastics should be encouraged, as valid alternative to common fossil-based plastics. In this view, the development of materials obtainable from renewable sources, characterized by minimum waste production, transport efficiency and controlled disposal and/or recycling after use, is constantly growing, as confirmed by the last market data.[2]

Moreover, in case of food packaging, the package should exhibit good mechanical properties and mainly high barrier performances, these last indispensable to prolong food shelf life. To this aim, nowadays, multilayered packaging dominates the market. However, the presence of different layers formed by different materials renders recycling a great challenge. In addition, recycling is further complicated by the contamination of the package with organic matter.

In this complex scenario, polyesters synthesized from 2,5-furan dicarboxylic acid can be considered very interesting candidates, due to their biobased nature together with outstanding mechanical and barrier

properties, making them particularly promising for the realization of recyclable monomaterial packages for food packaging applications.

In this contribution, poly(pentamethylene furanoate) PPeF (Figure 1) a new furan-based polyester, was synthesized by two-step melting polycondensation, a one-pot and solvent-free technique, and subjected to molecular and thermal characterization. Interestingly, although amorphous and rubbery at room temperature, PPeF could be processed in form of free-standing film. In terms of functional properties, PPeF shows exceptional barrier and mechanical response, which make it suitable for the production of flexible packaging (flexible films). More in details, the mechanical behavior was typical of elastomers, i.e. low elastic modulus and stress at break, high elongation at break together with an instant shape recovery after breaking, indicating the presence of net points.

In order to better understand the origin of these peculiar as well as outstanding properties, a further study combining calorimetric, diffractometric and spectroscopic techniques was carried out. The results obtained evidenced the formation of a particular ordered microstructure, different from the classical crystalline phase, characterized by a lower degree of order (2-D, 1-D instead of 3-D), originating from a partially ordered arrangement of furan rings, favored by intermolecular hydrogen bonds. The existence of such interchain interactions has been proved also through broadband dielectric spectroscopy ad-hoc experiments.

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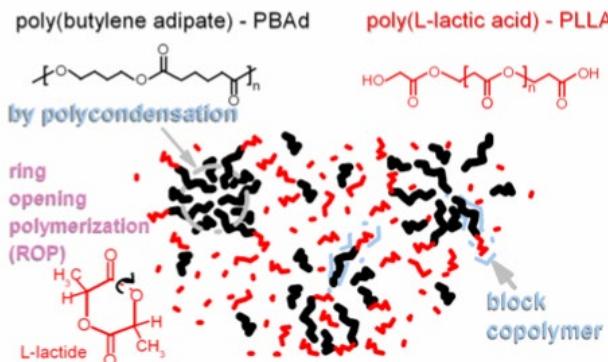


Figure 1. Chemical structures of PLLA, PBAd and their copolymers.

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## Synthesis, characterization and thermo-dynamical study of block copolymers based on poly(butylene adipate) and poly(L-lactic acid) for drug delivery applications

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Bio-based and biodegradable aliphatic polyesters, such as poly(L-lactide), poly( $\epsilon$ -caprolactone), poly(alkylene succinate)s, polyglycerol hyperbranched polyesters etc. serve as excellent “green” candidates for a broad range of applications (biomedical, pharmaceutical, agricultural and industrial), combining biocompatibility, renewability and generally good performance.

Poly(lactic acid) (PLA), the polymer of interest here, is a commercially available, bio-based synthetic polymer, widely used in biomedical applications due to its biocompatibility, biodegradability and its excellent physicochemical and mechanical properties. However, its high hydrophobicity as well as the low degradation rate, originating from its high degree of crystallinity, are often considered shortcomings in terms of drug delivery. Thus, blending, chemical modification, composite technology, and novel fabrication technology are being developed to improve its performance. The attractive properties of aliphatic polyesters derived from dicarboxylic acids and different aliphatic diols

[such as poly(butylene adipate) (PBAd)] render them ideal materials for the preparation of depot pharmaceutical formulations [1], and an interesting alternative in an attempt to confront the aforementioned drawbacks of PLA.

The present work describes the synthesis of poly(butylene adipate) (PBAd), by melt polycondensation, poly(L-lactic acid) (PLLA), by ring opening polymerization, and the novel block copolymers PLLA/PBAd in ratios 90/10, 95/5, 75/25 and 50/50 (Figure 1). The prepared aliphatic polyesters were characterized by a combination of techniques (NMR and FT-IR spectroscopy, X-ray diffraction, calorimetry, polarized optical microscopy etc.). The overall data showed that the different copolymer composition results directly in severe changes in the polymer crystals distribution and that the semicrystalline morphology can be tuned to a wide extend. The latter makes these systems quite promising for drug delivery applications.

### References

- [1] S. Nanaki, P. Barmpalexis, Z. Papakonstantinou, E. Christodoulou, M. Kostoglou and D. N. Bikaris, Journal of Pharmaceutical Sciences, 2018, 107, 1–11.



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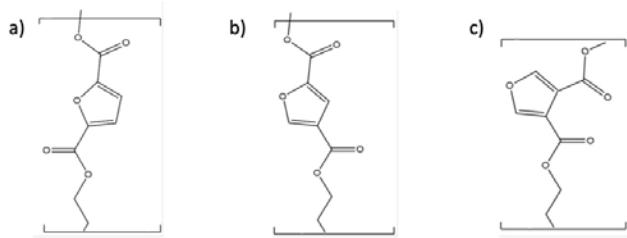
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## Structure and Properties of Polymers from combined Vibrational Spectroscopy and Atomistic DFT Simulations

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The atomistic view of the polymer structure – in particular, its conformational preferences, sequential distribution of non-symmetrical monomeric units and chain-to-chain intermolecular interactions - is of utmost relevance for a rational understanding of the structure-properties relationship ruling potential applications of the polymer.

In recent works,[1,2] the structure and dynamics of ethylene furandicarboxylate-based polymers (PEF, Fig. 1) have been addressed by combining vibrational spectroscopy (Raman, Infrared, and Inelastic Neutron Scattering (INS) spectroscopies) with DFT calculations.

For 2,5-PEF, [1] results show that in the amorphous domains, where intermolecular interactions are weak, PEF chains favor a helical conformation. Prior to crystallization, polymeric chains undergo internal rotations extending their shape in a zigzag pattern – an energetically unfavorable geometry which is stabilized by C-H...O bonds among adjacent chain segments. The energy difference among the amorphous and crystalline chains of PEF is higher than in PET poly(ethylene terephthalate) and contributes to PEF's higher crystallization temperature.

In 2,4-PEF polymer, [2] the crystallization is hampered by the 2,4-FDCA monomer asymmetry. A combination of Inelastic Neutron Scattering and DFT calculations has been used to assess the conformational and regiochemistry preferences of this polymer. It polymerizes following a random distribution of monomer orientation, thereby rendering the formation of periodic interchain C-H...O contacts wholly unfeasible, and ultimately favoring the formation of randomly coiled chains based on gauche ethylene glycol (EG) segments. In the absence of C-H...O stabilization the ordered crystalline arrangement is disfavored and polymer chains - adopting several quasi iso-energetic structures - prefer to solidify into an amorphous mess.

Preliminary DFT calculations on 3,4-PEF show the importance of the non-planarity of the 3,4-FDCA monomer. Steric hindrance between carboxylate groups yields a ca. 15–25° out-of-plane distortion of the carboxylate groups, with remarkable effects on the polymer chain structure.

## References

- [1] C.F. Araujo, M.M. Nolasco, P.J.A. Ribeiro-Claro, S. Rudć, A.J.D. Silvestre, P.D. Vaz, and A.F. Sousa, *Macromolecules*, 2018, 51, 3515–3526. DOI: 10.1021/acs.macromol.8b00192
- [2] M.M. Nolasco, C. F. Araujo, S. Thiagarajan, S. Rudić, P.D. Vaz, A.J.D. Silvestre, P.J.A. Ribeiro-Claro, A.F. Sousa, *Macromolecules*, 2020, 53, 1380-1387. DOI: 10.1021/acs.macromol.9b02449.



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## FUR4Sustain: moving from on-line implementing to jointly obtained results

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As no clear evidence on when and how we will be able to overcome the effect pf pandemic period, a clever demarche consists in finding ways to achieve our objectives in quasi-normal conditions of live. That is why my presentation deals with Romanian partner's expectations from the other project partners and with our offer meant to change our manner to work together.

### What we need?

As partners with expertise in polymer science and inorganic materials /soft materials and combinations between them ((nano) composites, hybrids) [1] we need monomers with different structures from WG1 partners. The monomers can be sent by postal services as samples without commercial value and intended only for use in the research laboratory.

### Our offer

Details on the following aspects will be presented:

- Synthetic approaches up to laboratory scale technologies for the preparation of different kind of furan (tetrahydrofuran)-based polymers (polyesters, polyamides, polyurethanes) or functional macromers to be further used as precursors in the preparation of more complex polymer structures (block/graf copolymers, crosslinked structures, interpenetrating networks ...);
- Use of furan monomers/furan-based polymers in the preparation of mesoporous carbon [2];
- A deep characterization of structure, morphology and properties of the polymers/polymeric materials prepared either by us or by other WG3 partners (see the available equipment on eeris platform) [3].

”

### References

- [1] <https://www.icmpp.ro/publications.php>
- [2] Huang, A., Zhu, X., Wang, S., Tian, Y., & Wang, X. (2016). Synthesis of bimodal mesoporous carbon spheres from biomass starch and CBZ release. Materials Letters, 169, 54–5
- [3] short link: <https://eeris.eu/ERIF-2000-000Z-0217>



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## Polybutylene succinate biocomposites for wood-mimic applications

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Benefits of introducing cellulose nanoparticles in polymer matrix are well known. We will present herein a several polymer biocomposite materials with wood-mimic containing only bio-based and biodegradable components. Polybutylene succinate, as a biodegradable aliphatic polyester derived from renewable resources, has potential being completely bio-based and biodegradable. Cellulose filler from various waste products and sources could be very efficient filler. Wood-mimic biocomposites have been prepared by functionalization of cellulose micro- and nanofibers and compatibilization with matrix.

Thermal, tensile, viscoelastic, rheological and biodegradation properties could be controlled by functionalization of the cellulose filler and by choosing optimal blending strategy. These composites showed some wood-mimic properties and could be used as good alternative to conventional wood plastic composites from fossil resources based polyolefin polymers.

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### References

- [1] O. Platnieks, A. Barkane, N. Ijudina, G. Gaidukova, V.K. Thakur, S. Gaidukovs, J Clean Prod, 2020, 270, 122321.
- [2] O. Platnieks, S. Gaidukovs, A. Barkane, N. Ijudina, A. Sereda, G. Gaidukova, L. Grase, V.K. Thakur, I. Filipova, V. Fridrihsone, M. Skute, M. Laka, Polymers, 2020, 12 (7), 1472, 1-20.
- [3] O. Platnieks, S. Gaidukovs, A. Barkane, N. Ijudina, A. Sereda, G. Gaidukova, L. Grase, V.K. Thakur, I. Filipova, V. Fridrihsone, M. Skute, M. Laka, Molecules, 2020, 25 (1), 121.



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Let's connect for furan based chemicals  
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