Novel packaging films and textiles with tailored end of life and performance based on bio-based copolymers and coatings.

D.1.2 Survey of commercial biopolymers, additives & monomers and strategy for further improvement needed

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Acronyms

WP	Work Package
D	Deliverable
EU	European Union
EC	European Commission
BBI-JU	Bio-Based Industries Joint Undertaking
H2020	Horizon 2020
PLA	Polylactic acid
LA	Lactic acid
SA	Succinic acid
IA	Itaconic acid
AA	Adipic acid
GlucA	Glucaric acid
GlutA	Glutamic acid
FA	Fumaric acid
TA	Tartaric acid
MA	Malic acid
GA	Glycolic acid
AsA	Aspartic acid
FDCA	Furandicarboxylic acid

Executive summary

One of the BIOnTop's main goals is the fabrication of new polylactic acid (PLA) based materials with tailored properties including the end of life (EoL) properties. In order to achieve these objectives, the strategy selected within BIOnTop consists in the synthesis of PLA copolymers employing different diacids. Bio-sourced additives, fillers and coatings will be also employed during the project to further design and tailor the desired properties of the final products. Thus, Deliverable D1.2 consists of a survey of commercial grades from different suppliers of the biopolymer PLA of interest for the project. Available diacids for copolymerisation and coating formulations, with special emphasis on diacids produced from bio-sources are listed as well. In the same way, a comprehensive search for selected additives and natural fillers that can be extracted from biomass is reported.

Introduction

In order to achieve BIOnTop's goal of producing innovative new biopolymers for copolymerisation and coating formulations to be applied on different packaging applications, a survey of commercially available biomaterials is needed. These brand-new biomaterials will be fabricated with the goal of tailoring their end of life properties so the final packaging product would be either recyclable or home-compostable depending on the final application of the mentioned packaging. Thus, polylactic acid was the base biopolymer of choice and the synthesis of copolymers employing bio-sourced diacids was selected as the way of modifying and tailoring its properties (including its biodegradability properties). PLA will be used within BIOnTop for further formulation of blends and as the benchmark reference material which the final properties of the new bio-based packaging products will be compared to as well. Since BIOnTop strategy consists in fabrication of new PLA based copolymers employing bio-based diacids, performing a survey of the possible available diacids for polymerization as well as additives and fillers is crucial in order to achieve the results that will make BIOnTop successful. We report herein a comprehensive survey of bio-based materials including suppliers and costs with the aim of selecting the starting materials to be employed to start formulation work at lab scale in WP2 and 3.

1. Survey of commercially available materials

1.1 Survey of PLA producers and pure and blended grades available in relevant quantities

Polylactic acid is an aliphatic polyester that can be synthesized by either lactic acid or lactide. Lactic acid, or 2-hydroxypropanoic acid, present hydroxyl and carboxylic acid functionalization that can lead to intermolecular esterification reactions. Self-esterification of lactic acid at 120-135 ºC leads to formation of the cyclic dimer lactide, or 6-dimethyl-1,4-dioxane-2,5-dione, which is insoluble in water. These two monomers present respectively one and two stereo centres and thus are present in nature in the two enantiomeric forms (L- or D) or, in the case of lactide, *R,R*/*S,S*/*R,S* diastereoisomers. Polylactic acid obtains a mouldable stereochemical structure that may be easily modified by controlling the ratio of its L- or D-isomers during the polymerization. Indeed, generally PLA is a copolymer constituted by poly(L-lactic acid) (PLLA), which confers crystallinity to the structure, and poly(D,L-lactic acid) (PDLLA), which leads to amorphous polymers.

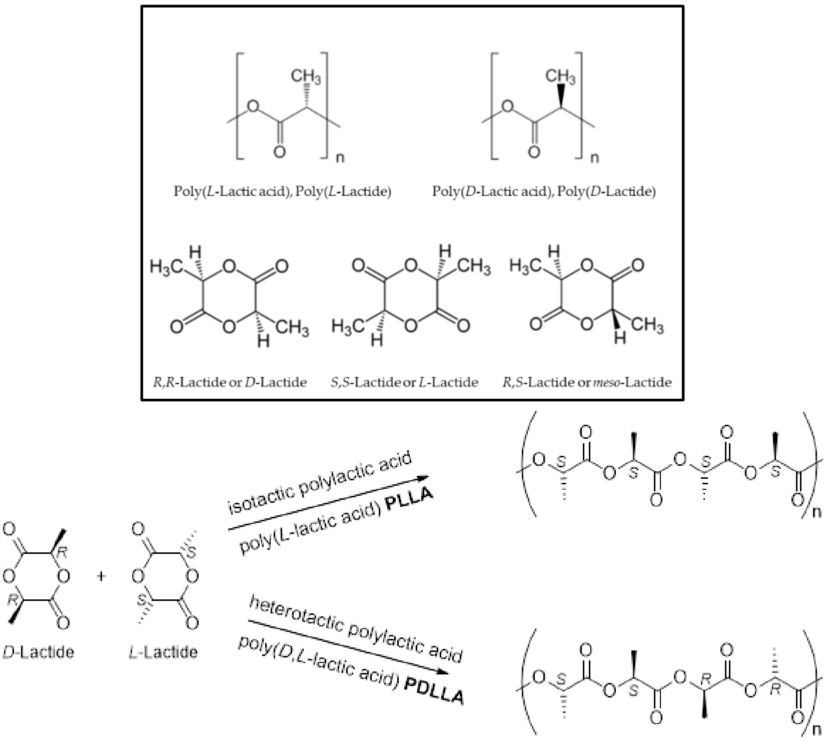

Figure 1. PLA monomers and polylactic acid with different tatcitities

There are currently three producers that offer Polylactic acid neat resin commercially. Below is a list of the producers and the commercial PLA neat resins they offer to the market. JILIN Cofco Biomaterials has started up production of its 10 kton per year PLA plant end of 2018, but unfortunately at the moment, no public information is available on the PLA grades they are offering.

Table 1. Commercially available PLA grades.

Producer	PLA Grade	Description
Total Corbion PLA	Luminy® L105	High flow resin suitable for thin wall injection molding
	Luminy® L130	Medium flow resin suitable for injection molding and fiber spinning
	Luminy® L175	High viscosity resin suitable for film extrusion, thermoforming or fiber spinning
	Luminy® LX530	Medium flow fiber-grade resin suitable for staple fiber or spunbond applications
	Luminy® LX575	High viscosity resin suitable for extrusion processes.
	Luminy® LX930	Medium flow resin suitable for use as low melting component in sheath-core configuration
	Luminy® LX975	High viscosity resin suitable for use as a heat-seal layer in film applications
	Luminy® D070	Medium viscosity PDLA resin for use in full stereocomplex PLA compounds
	Luminy® D120	General purpose nucleating agent for high heat PLA resins
Natureworks	Ingeo® 2003D	Used as is or as part of a formulated blend on conventional extrusion equipment
	Ingeo® 2500HP	High viscosity & designed to crystallize during processing for extrusion
	Ingeo® 3001D	Unlubricated, medium-flow grade for injection molding
	Ingeo® 3052D	Lubricated, medium-flow grade for injection molding
	Ingeo® 3100HP	Medium viscosity & designed for medium-flow injection molding applications
	Ingeo® 3251D	Lubricated, ultra high flow grade for injection molding

	Ingeo® 3260HP	Designed to crystallize during processing for higher heat deflection temps in opaque applications
	Ingeo® 4032D	High heat film
	Ingeo® 4043D	General purpose film
	Ingeo® 4044D	Reactive extrusion grade
	Ingeo® 4060D	Heat seal layer for film
	Ingeo® 6060D	Amorphous low melt for staple fiber/bico fiber sheath layer 3.5 Relative Viscosity (RV)
	Ingeo® 6100D	For when lower fiber shrinkage and higher dimensional stability is required
	Ingeo® 6201D	Continuous filament/staple for dyed fiber applications
	Ingeo® 6202D	Staple fiber/spunbond for nonwovens, non-dyed fiber applications
	Ingeo® 6252D	Meltblown
	Ingeo® 6260D	Designed for meltblown fiber processing or extrusion into mechanically drawn staple fibers
	Ingeo® 6302D	Amorphous low melt for staple fiber/bico fiber sheath layer 3.0 RV
	Ingeo® 6362D	Higher melt flow resin designed for specialty fiber products where an amorphous structure is desired
	Ingeo® 6400D	Monofilament/BCF/Industrial multifilament products
	Ingeo® 6752D	Sheath polymer for spunbond applications
	Ingeo® 7001D	General purpose ISBM bottle grade
	Ingeo® 7032D	Heat-set ISBM bottle grade
	Ingeo® 8052D	Expanded foam sheet
	Ingeo® 3D450	3D Printing Monofilament Break-away Support Grade

	Ingeo® 3D850	Fast crystallizing, low color grade designed for 3D printing monofilaments -- recommended for investment casting
	Ingeo® 3D870	High heat & impact resistance grade 3D printing monofilament used in industrial applications
Zhejiang Hisun Biomaterials	REVODE® 101	Transparent extrusion grade, mainly used for laminating, blend film, etc
	REVODE® 110	Transparent Extrusion grade, mainly used for (BO) film applications
	REVODE® 190	Higher melting point extrusion grade resin, used for extrusion blow molding, spinning and other purposes
	REVODE® 210	Transparent injection molding grade with properties similar to REVODE 110, but with higher flow for injection molding
	REVODE® 290	High melting point injection grade resin, used for transparent injection molding products and injection stretch blow molding products

1.2 Survey of available diacids for copolymerisation and coating formulations

Dicarboxylic acids are organic molecules having two carboxylic residues; α,ω-, linear, aliphatic dicarboxylic acids have the functional groups separated by a defined number of methylene groups. Figure 2 reports the structure of adipic acid (1,6-dicarboxyexanoic acid) as a typical example of this class of molecules: adipic acid is the example of an α,ω-dicarboxylic acid bearing a linear aliphatic four methylene chain.

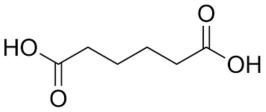

Figure 2. Chemical structure of adipic acid (1,6-dicarboxyexanoic acid)

Generally speaking, dicarboxylic group is a very polar, due to the presence of two oxygen atoms, having higher electronegativity than carbon atoms. However, the longer the aliphatic chain, the lower the polarity of the molecule, due to the shield effect of the methylene chain. Indeed, adipic acid, having four methylene groups, shows moderate solubility in water at 25 °C (30 g/L) while suberic acid (1,8-octanedioic acid), having two more methylene groups than adipic acid, shows reduced solubility in water (11 g/L).[1]

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[1] Source: Pubchem.ncbi.nlm.nih.gov

Dicarboxylic acids are often used in polycondensation reactions, together with diols, to give polyesters.[2] A 1:1 dicarboxylic acid: diol molar ratio has to be applied to obtain high molecular weight products, as described in the kinetics of step reactions. The reaction usually takes place in two steps: the first one, the transesterification step, gives oligomers, while the second, the real polycondensation step, usually gives high molecular weight products. The second step is usually carried out under vacuum (0.1 mbar), to remove small molecules such as water or low molecular weight alcohols that form and therefore to shift the equilibrium reaction towards high molecular weight products. Polycondensations are performed either in solvents and in the melt, the latter one being preferred for pilot scale and industrial scale applications. Transesterification catalysts, such as titanium (IV) tetrabutoxide, are usually applied.[2]

Copolymers of polylactic acid (PLA) introducing different monomers such as dicarboxylic acids (DA) within the polylactic acid polymer chains show lower crystallinity leading to enhanced biodegradability properties. Furthermore, copolymerization makes possible the customization of different properties such as different copolymer chain lengths and molecular weight distributions, thus providing a good approach for tuning the biodegradation of the final compounds. Biodegradability of the aimed copolymers will be easily tunable since the presence of monomer units lacking methyl groups in alpha position to the ester moiety favours biodegradability by allowing an easier access of the microorganisms to the carbonyl groups.

Many α,ω-dicarboxylic acids, having linear structure and an even number of carbon atoms, are all commercially available. Indeed, oxalic (1,2-etanedioic acid), succinic acid (1,4-dicarboxybutanoic acid), adipic acid (1,6-dicarboxyexanoic acid) as well as suberic acid (1,8-octanedioic acid) and sebacic acid (1,10 -decanedioic acid) are indeed purchasable form many chemical industries, starting from Sigma-Aldrich. Representative examples of suppliers[3] of α,ω-dicarboxylic acids having even number of methylene groups between the two functional groups are reported in Table 2.

Table 2. Representative suppliers of α,ω–dicarboxylic acids having an even number of carbon atoms

Name	Formula	CAS	Supplier	Country
Oxalic acid	$C_2O_4H_2$	144.62.7	Parchem Europe	Europe
			CBC Europe	Germany
			Moeller Chemie GmbH &Co.	Germany
			F.B. Sielbermann GmbH	Germany
			S3 Chemicals	Germany
Succinic acid	$C_4H_6O_4$	110.15.6	Dr. Spiess Chem. Fabrik. GmbH	Germany
			Midas Pharma	Germany
			Galactic Innovation	Belgium
			Peter Greven GmbH	Germany

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[2] (a) Signori, F.; Solaro, R.; Chiellini, E.; Lips, P.A.M.; Dijkstra, P.J.; Feijenet, J. Synthesis and characterization of segmented poly(ether ester)s containing H-bonding units. *Macromol. Chem. Phys.*, **2003**, *204*, 1971 – 1981. (b) Signori, F.; Solaro, R.; Lips, P.A.M.; Dijkstra, P.J.; Feijen, J.; Chiellini, E. Segmented multifunctional poly(ether ester) polymers containing H-bonding units. Preparation and characterization. *Macromol. Chem. Phys.*, **2004**, *205*, 1299 – 1308.

[3] Source: industrystock.com

			Emery Oleochemicals GmbH	Germany
Adipic acid	$C_6H_{10}O_4$	124.04.9	Bayer	Germany
			MCC-Mennsig Chemiehandel &Consultant GmbH	Germany
			Kraus Chemie e.K.	Germany
			S3 Chemicals	Germany
			BAK Handelsbetrieb	Germany
Suberic acid	$C_8H_{14}O_4$	505.48.6	Wuhan Atomole	China
			AcrosOrganics	U.S.
			ChemPure	Germany
Sebacic acid	$C_{10}H_{18}O_4$	111.20.6	Parchem Europe	Europe
			Banner Chemicals	U.K.
			Arkema Europe	Europe
Malic acid	C4H6O5	97-67-6	TER chemical distribution	Germany
			Dr. Spiess Chem. Fabrik GmbH	Germany
			CG Pharma and nutrition	Germany

Note that α,ω-diacids, having an odd number of carbon atoms (malonic, glutaric, pimelic, azelaic acids), even if commercially available, usually have higher price.

The US Department of Energy identified 12 strategic building block chemicals that can be produced from carbohydrates or sugars via biological or chemical conversions from biomass.[4] Most of them are bifunctional dicarboxylic acids such as itaconic acid, adipic acid, glucaric acid, glutamic acid, fumaric acid, tartaric acid, malic acid, succinic acid, glycolic acid, aspartic acid and furandicarboxylic acid (Figure 3). These substances are potential candidates for the copolymerization with lactic acid (or lactide) to obtain materials presenting tailor-made biodegradability properties. All of them, except glycolic acid, are bio-produced at low cost.

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[4] Werpy, T.; Petersen, G. (2004) Top value added chemicals from biomass, vol 1. U.S. Department of Energy, Oak Ridge.

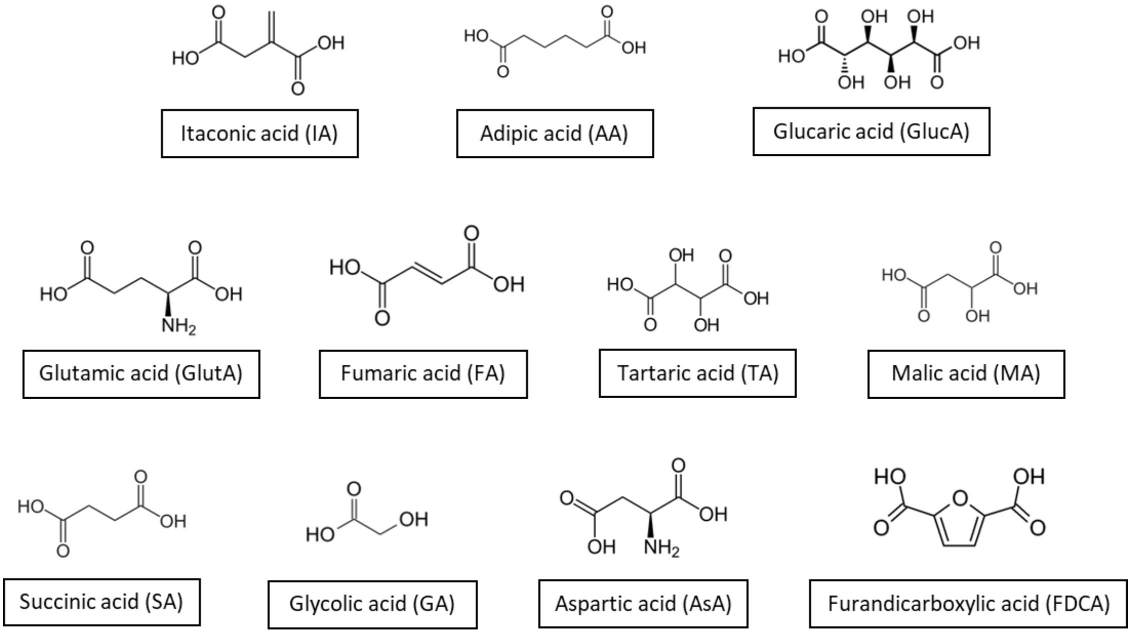

Figure 3. Bifunctional dicarboxylic acids that can be produced from carbohydrates or sugars *via* biological or chemical conversions from biomass.

- **Itaconic acid (IA):**

Itaconic acid, also known as methylene succinic acid, is a naturally occurring, non-toxic dicarboxylic acid which was traditionally obtained by distillation of citric acid, but it is nowadays produced, on an industrial scale, *via* bio-based fermentation of carbohydrates by *Aspergillus terreus*. This dicarboxylic acid is a white solid that is soluble in water, and polar organic solvents and it is used as an important building block in the chemical industry for the production of lubricants, as a co-monomer in the production of acrylonitrile-butadiene-styrene and acrylate latexes (with applications in the paper and architectural coating industry), to produce resins for coatings, thickeners, some herbicides and in medical applications. It has been intensively studied as an alternative co-monomer for acrylic acid and methacrylic acid in order to obtain renewable polyesters with enhanced functionality.[5] In the literature, co-polyesters based on itaconic acid and lactic acid have been also investigated for the synthesis of biodegradable hydrogels for drug delivery purposes.[6] Concerning the obtention of copolymers with lactic acid, Okuda *et al.* performed Sn-catalyzed ring opening polymerization reaction (ROP) of IA with PLA to produce IA-PLA macromonomers. The vinyl functionality present in the IA moieties was available for subsequent radical reaction leading to graft copolymers.[7]

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[5] Robert, T.; Friebel, S. Itaconic acid – a versatile building block for renewable polyesters with enhanced functionality. *Green Chem.*, **2016**, *18*, 2922 – 2934.

[6] (a) Grupta, V.K.; Sood, S.; Agarwal, S.; Saini, A.K.; Pathania, D. Antioxidant activity and controlled drug delivery potencial of tragacanth gum-cl-poly(lactic acid-*co*-itaconic acid) hydrogel. *Int. J. Biol. Macromol.*, **2018**, *107*, 2534 – 2543. (b) Sood, S.; Gupta, V.K.; Agarwal, S.; Dev, K.; Pathania, D. Controlled release of antibiotic amoxicillin drug using carboxymethyl cellulose-cl-poly(lactic acid-*co*-itaconic acid) hydrogel. *Int. J. Biol. Macromol.*, **2017**, *101*, 612 – 620.

[7] Okuda, T.; Ishimoto, K.; Ohara, H.; Kobayashi, S. Renewable biobased polymeric materials: facile synthesis of itaconic anhydride-based copolymers with poly(*L*-lactic acid) grafts. *Macromolecules*, **2012**, *45*, 4166 – 4174.

Regarding biodegradability, the methylene group present in the itaconic acid structure would hinder the hydrolysis process in a similar way as in the case of the methyl group in the lactic acid moieties but the pending double bond is more difficult to be broken. On the other hand, the presence of two different monomers difficult the crystallization, enhancing the polymer biodegradability.

Most of IA suppliers are based in China and there are only a few producers in Europe such as Itaconix (UK) and Akzo Nobel (Neth.) and DSM.

- **Adipic acid (AA):**

Adipic acid (hexanedioic acid) is an industrially very important building block used in the production of nylon, polyurethanes, plasticizers and lubricants. About 60 % of the 2.5 billion kg of adipic acid produced annually is used as monomer for the production of nylon 6,6 by a polycondensation reaction with hexamethylenediamine. Adipic acid is also widely used as a plasticizer for the production of polyvinyl chloride (PVC) and polyvinylbutyral (PVB), and as an approved additive in the chemical, pharmaceutical and food industries. It is conventionally synthesized from benzene, which is first transformed into cyclohexane, then into cyclohexanone and cyclohexanol, which are then converted into adipic acid. Adipic acid can be produced in high yields from biobased muconic acid,[8] glucaric acid,[9] and succinic acid.[10]
Polyesterdiols and polyestercarbonatediols of adipic acid has been reported to be employed for the polymerization of lactide giving rise to copolymers of PLA.[11] Poly(butylene adipate)[12] and poly(ethylene adipate)[13] telechelic prepolymers have been employed for the synthesis of PLA copolymers adipic acid copolymers either by polycondensation or by ring opening polymerization reactions, respectively. Hichem *et al.*, synthetized poly(ethylene adipate-*co*-*D*,*L*-lactic acid) copolymers and submitted them to in vitro biodegradation analysis. The results indicated that the copolymer degradation rate increased with increasing adipate content.[14]

Companies that industrially produce adipic acid by conventional chemical methods are Invista, Ascend, and Honeywell in USA, BASF in Germany, Radici in Italy, and China Shenma and PetroChina in China. Bio-based adipic acid is not currently mass produced, but still at the R&D stage. Nevertheless, there are several companies involved in bio-adipic acid projects, especially in North America, and some have reached pilot scale. Thus, in recent years, Rennovia, Verdezyne, BioAmber, DSM, Celexion, and Genomatica developed new processes for the production of bio-based adipic acid scales. Especially, the Rennovia’s process was suggested to be highly cost competitive with the conventional DuPont/Invista cyclohexane-based oxidation process.

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[8] Niu, W.; Draths, K.M.; Frost, J.W. Benzene-free synthesis of adipic acid. *Biotechnol. Prog.*, **2002**, *18*, 201 – 211.

[9] Boussie, T.R.; Dias, E.L.; Fresco, Z.M.; Murphy, V.J.; Shoemaker, J.; Archer, R.; *et al*. Production of adipic acid and derivatives from carbohydrate-containing materials. *Google Patents* **2014**.

[10] Cheng, K.-K.; Zhao, X.-B.; Zeng, J.; Zhang, J.-A. Biotechnological production of succinic acid: current state and perspectives. *Biofuels, Bioprod. Biorefin.*, **2012**, *6*, 302 – 318.

[11] Florjanczyk, Z.; Jozwiak, A.; Kundys, A.; Plichta, A.; Debowski, M.; Rokicki, G.; Parzuchowski, P.; Lisowska, P.; Zychewicz, A. Segmental copolymers of condensation polyesters and polylactide. *Polym. Degrad. Stabil.*, **2012**, *97*, 1852 – 1860.

[12] Hiltunen, K.; Harkonen, M.; Seppala, J. V.; Vaananen, T. Synthesis and characterization of lactic acid based telechelic prepolymers. *Macromolecules*, **1996**, *29*, 8677 – 8682.

[13] Liu, J.; Chen, P.; Li, J.; Jiang, S.-H.; Jiang, Z.-Q.; Gu, Q. Synthesis of poly(ethylene adipate-*co*-*L*-lactic acid) copolymers *via* ring opening polymerization. *Polymer Bulletin*, **2011**, *66*, 187 – 197.

[14] Hichem, B.; Kaddour, G.; Imene, B. Synthesis and in vitro biodegradation of poly(ethylene adipate-*co*-*D*,*L*-lactic acid) copolymers (PLEA). *Orient. J. Chem.*, **2014**, *30*, 1061 – 1069.

- **Glucaric acid (GlucA):**

Glucaric acid, also known as saccharic acid, is the product of the oxidation of sugars or polysaccharides with nitric acid. This reaction was first reported by German chemist Heinrich Kiliani in 1925. GlucA is the dicarboxylic acid derived from *D*-glucose in which both the aldehydic carbon atom and the carbon atom bearing the primary hydroxyl group are oxidized to carboxylic acid groups. Its disodium salt is used as a chelating agent in dishwasher detergents replacing environmentally problematic phosphates in most cases. Glucaric acid is a potentially important building block for the synthesis of polyamides or hyperbranched polyesters but, to our knowledge, no synthesis of glucaric acid/PLA copolymers has been reported so far.

Rivertop Renewables has manufactured glucaric acid since 2015 by a modification of the conventional process consisting in a one-pot oxidation process without NOx release. Rennovia and Johnson Matthey have operated a small-scale plant at Matthey's Stockton, England, R&D center since 2015 and in February of 2017 licensed their jointly developed glucaric acid manufacturing technology to Archer Daniels Midland. Their process consists of a catalytic aerobic oxidation.

- **Glutamic acid (GlutA):**

Glutamic acid is a non-essential α-amino acid that is used by almost all living beings in the biosynthesis of proteins. Glutamate anion is also responsible for the savory flavor and it is used in glutamate flavorings such as monosodium glutamate (MSG).

Synthesis of polyamides from glutamic acid (polyglutamates) is very well know and developed industrially. If the amine group of the amino acid is protected, polyesters can be prepared in the presence of diols.[15] There are several examples of polylactic polyglutamic copolymers described in literature.[16]

- **Fumaric acid (FA):**

Fumaric acid or *trans*-butenedioic acid is a naturally occurring metabolite, which is found in the Krebs cycle and contains a *trans*-configurated double bond. It is formed by the oxidation of succinic acid by succinate dehydrogenase and it is converted by the enzyme fumarase to *L*-malate. Fumaric acid is used to make plastics and paints, in food processing and preservation, among other uses. The development of fumarate-based polyesters for biomedical applications started around 30 years ago. The presence of the double bond in its chemical structure makes fumaric acid a candidate building block for crosslinkable polymers. The first and most comprehensively investigated fumarate-based copolymer is the biodegradable copolyester poly(propylene fumarate) (PPF). PPF polyester was first polymerized from

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[15] See, for example: Tadros, R. M.; Noureddini, H.; Timm, D. C. Z-protected glutamic acid-based biodegradable thermoplastic and thermosetting polyesters: Synthesis and characterization. *J. Appl. Polym. Sci.*, **1999**, *73*, 869 – 879.
[16] See, for example: (a) Zhang, G.; Zhang, R.; Wen, X.; Li, L.; Li, C. Micelles based on biodegradable poly(*L*-glutamic acid)-*b*-polylactide with paramagnetic Gd ions chelated to the shell layer as a potential nanoscale MRI-visible delivery system. *Biomacromolecules*, **2008**, *9*, 36 – 42. (b) Deng, C.; Rong, G.; Tian, H.; Tang, Z.; Chen, X.; Jing, X. Synthesis and characterization of poly(ethylene glycol)-*b*-poly(*L*-lactide)-*b*-poly(*L*-glutamic acid) triblock copolymer. *Polymer*, **2005**, *46*, 653 – 659. (c) Deng, C.; Tian, H.; Zhang, P.; Sun, J.; Chen, X.; Jing, X. Synthesis and characterization of RGD peptide grafted poly(ethylene glycol)-*b*-poly(*L*-lactide)-*b*-poly(*L*-glutamic acid) triblock copolymer. *Biomacromolecules*, **2006**, *7*, 590 – 596. (d) Yang, Y.; Zheng, Y.; Zhuang, X.; Chen, X. Preparation and characterization of a new copolymer poly(*L*-glutamic acid)-*block*-poly(lactic-*co*-glycolic acid). *J. Control. Release*, **2011**, *152*, e192 – e269. (e) Guan, H.; Xie, Z.; Zhang, P.; Deng, C.; Chen, X.; Jing, X. Synthesis and characterization of biodegradable amphiphilic triblock copolymers containing *L*-glutamic acid units. *Biomacromolecules*, **2005**, *6*, 1954 – 1960.

fumaric acid and propylene oxide.[17] In the late 90s, the synthesis of PPF was performed employing fumaryl chloride and propylene glycol[18] and nowadays the synthesis of PPF consists of transesterification of diethylfumarate with propylene glycol and subsequent polycondensation of the diester intermediate bis(2-hydroxypropyl)fumarate.

- **Tartaric acid (TA):**

Tartaric acid is a dicarboxylic acid that can be found in many fruits, especially in grapes. Its monopotassium salt is generated during the winemaking process. Potassium bitartrate develops naturally in the process of winemaking. It is commonly mixed with sodium bicarbonate and is sold as baking powder used as a leavening agent in food preparation. The acid itself is added to foods as an antioxidant E334 and to impart its distinctive sour taste.

Tartaric acid and its derivatives have a plethora of uses in the field of pharmaceuticals. For example, it has been used in the production of effervescent salts, in combination with citric acid, to improve the taste of oral medications. The potassium antimonyl derivative of the acid known as tartar emetic is included, in small doses, in cough syrup as an expectorant. Tartaric acid also has several applications for industrial use. The acid has been observed to chelate metal ions such as calcium and magnesium. Therefore, the acid has served in the farming and metal industries as a chelating agent for complexing micronutrients in soil fertilizer and for cleaning metal surfaces consisting of aluminium, copper, iron, and alloys of these metals, respectively.

- **Malic acid (MA):**

Malic acid (2-hydroxybutanedioic acid) is a dicarboxylic acid bearing a linear aliphatic chain with a hydroxy functionality in position 2. It is a polar molecule, having complete solubility in water at 25 °C, due to the presence of the short aliphatic chain and of the polar hydroxyl group. In addition, the presence of the chiral centre determines two isomers, *L*- and *D*- malic acid (Figure 4).

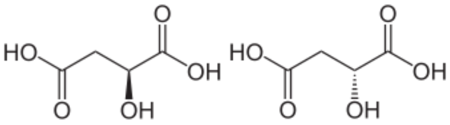

Figure 4. *L*- and *D*- malic acid (2-hydroxybutanedioic acid)

Companies such as Novozymes and Myriant have developed proprietary technologies based on aforementioned fermentation process. Currently, 80 % of global malic acid is produced synthetically and the remaining is produced by renewable sources among other from fruit waste, as done by OENO (collaborator of INSTM who will act as supplier for WP2). Commercialization of bio-based malic acid at competitive pricing as compared to its synthetic counterpart is expected to create immense opportunities to be used as platform chemical in the future. The estimated bio-based malic acid price is at around 2400 €/tonne. At the market price of 1.9 €/kg, MA production from soy molasses via PMA fermentation offers an economically competitive process. MA is used to produce bio-based polyesters which find application in pharmaceuticals used to treat cancer cells. It has been demonstrated that poly(malic acid-*co*-*L*-lactide) acts as a superb degradation accelerator for PLA in physiological conditions due to the superiority of poly(malic acid) vs. PLA to biodegrade.

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[17] Domb, A. J.; Laurencin, C. T.; Israeli, O.; Gerhart, T.N.; Langer, R. Formation of propylene fumarate oligomers for use in bioerodible bone cement composites. *J. Polym. Sci. A*, **1990**, *28*, 973 – 985.

[18] Peter, S.J.; Suggs, L.J.; Yaszemski, M.J.; Engel, P.S.; Mikos, A.G. Synthesis of poly(propylene fumarate) by acylation of propylene glycol in the presence of a proton scavenger. *J. Biomater. Sci. Polym. Ed*., **1999**, *10*, 363 – 373.

- **Succinic acid (SA):**

Nowadays, succinic acid is produced at a rate of 25,000 tons per year from maleic anhydride obtained by oxidation of the C4 fraction (n-butane or butadiene) of crude oil. However, the biotechnological production of SA by fermentation of carbohydrates has attracted recent attention. At larger scale (typically 50 kTonnes), and due to lower costs of raw materials, bio-SA has the potential to be cheaper than its fossil-derived product and is expected to open up new markets and applications. Reverdia and Myriant's production cost for bio-SA is estimated to be lower than 1,040 €/MT whereas market prices for petroleum-derived SA are reported between $ 6,000 and $ 9,000/MT. Building on such advantage, the most conservative market studies estimates 250 ktonnes of bio-based SA will be produced by 2020 with high opportunities for growth in EU. Some of the major companies dominating this market are Reverdia (AB), BioAmber and Succinity. As an example of copolymerization synthesis, lactic acid, ethylene glycol and succinic acid were copolymerised with different monomer feed ratios by direct polycondensation. The lack of methyl groups in the succinic molecule should favour the biodegradation and the biodegradation of its derivatives such as poly(butylene succinate) (PBS) are well demonstrated. In fact, PBS is home compostable according to Vinçotte certificate. For that reason, it is an interesting blend partner for PLA. However, most PBS on the market is not yet bio-based and its market is less established than that of PLA. Possibility of terpolymers with adipic acid are interesting solutions to be addressed too.

- **Aspartic acid (AsA):**

Aspartic acid is an α-amino acid that is used in the biosynthesis of proteins. Similar to all other amino acids it contains an amino group and a carboxylic acid. Its α-amino group is in the protonated –NH+ 3 form under physiological conditions, while its α-carboxylic acid group is deprotonated −COO− under physiological conditions. Aspartic acid has an acidic side chain (CH2COOH) which reacts with other amino acids, enzymes and proteins in the body. Under physiological conditions (pH 7.4) in proteins the side chain usually occurs as the negatively charged aspartate form. It is a non-essential amino acid in humans, meaning the body can synthesize it as needed. Aspartic acid, like glutamic acid, is classified as an acidic amino acid, with a pKa of 3.9, however in a peptide this is highly dependent on the local environment and could be as high as 14.

As of 2014, the global market for aspartic acid is $ 117MM annually (50 – 60 K MT/Year) with potential areas of growth accounting for an addressable market of $ 8.78 BB. The three largest market segments include the U.S., Western Europe, and China. Current applications include biodegradable polymers (polyaspartic acid), low calorie sweeteners (aspartame), scale and corrosion inhibitors, and resins. Nearly all aspartic acid is manufactured in China. Superabsorbent polymers One area of aspartic acid market growth is biodegradable superabsorbent polymers (SAP). Around 75 % of superabsorbent polymers are used in disposable diapers and an additional 20 % is used for adult incontinence and feminine hygiene products. Polyaspartic acid is a biodegradable substitute to polyacrylate.

- **Furandicarboxylic acid (FDCA):**

2,5-Furandicarboxylic acid is a bifunctional dicarboxylic acid containing an aromatic moiety that can be produced from certain carbohydrates. Since it can be produced by renewable sources, it has been therefore identified as one of the priority chemicals for establishing the "green" chemistry industry of the future. 2,5-Furandicarboxylic acid has been envisioned as a substitute for terephthalic acid in the production of polyesters such as polyethylene terephthalate (PET) and other current polymers containing aromatic moieties.

1.3 Survey of available additives

PLA's thermo-mechanical properties, as well as stability and processability, are usually tailored by means of different additives. Since PLA is a rigid and fragile polymer material, plasticizers are often used to enhance ductility. Either low molecular weight molecules, such as tributyl acetyl citrate,[19] and high molecular weight materials, such as poly(butylene adipato-*co*-terephthalate) PBAT[20] have been extensively used as PLA plasticizers. The major drawback of the addition of a plasticizer, however, is the shift towards lower temperature of the material glass transition, Tg, which appears at 55 – 60 °C in the pure PLA. This effect strongly limits the use of PLA at temperatures higher than room temperature. To overcome this drawback, nucleants and strengthening agents are added to improve polymer crystallinity and therefore hardness and resistance, to control viscosity of the melt polymer and to enhance its thermal and hydrolytic resistance. Inorganic substances, such as talc or calcium carbonate are often used as nucleating agents for PLA. In addition, organic LAK301 by Takemoto[21] worked efficiently as nucleating agent for PLA resin. Among all the bio-based available plasticizers for PLA, tributyl acetyl citrate, dimethyl sabacate and oligomer of lactic acid (OLA) have been chosen as representative samples.

Table 3. Representative suppliers of additives for PLA and biobased polyesters

Name	Formula	CAS	Supplier	Country
Acetyl tributyl citrate (atbc)	$C_{20}O_{34}H_{8}$	77-90-7	Vertellus (citroflex A4)	USA
			Long Range Europe	U.K.
			Pfizer Pharma GmbH	Germany
			Technosintesi SpA	Italy
Triethyl citrate			Vertellus (citroflex 2)	USA
Tributyl citrate			Vertellus (citroflex 4)	USA
Acetyltriethyl citrate			Vertellus (citroflex A2)	USA
n-butyril tri-n-hexyl citrate			Vertellus (citroflex B6)	USA
Dimethyl sebacate	$C_{12}H_{22}O_{4}$	106-79-6	Arkema Europe	Italy
			Parchem Europe	U. K.
			Henano GP chemicals	China
Oligo Lactic acid			Condensia Quimica	Spain
LAK			Takemoto	Japan

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[19] Coltelli, M.B.; Della Maggiore, I.; Bertoldo, M.; Signori, F.; Bronco, S.; Ciardelli, F. Poly(lactic acid) properties as a consequence of poly(butylene adipate-*co*-terephthalate) blending and acetyl tributyl citrate plasticization. *J. Appl. Polym. Sci.*, **2008**, *110*, 1250 – 1262.

[20] Signori, F.; Coltelli, M.B.; Bronco, S. Thermal degradation of poly(lactic acid) (PLA) and poly(butylene adipate-*co*-terephthalate) (PBAT) and their blends upon melt processing. *Polym. Degrad. Stabil.*, **2009**, *94*, 74 – 82.

[21] Source: takemoto.co.jp

1.4 Survey of natural fillers

The addition of rigid reinforcements (rigid particulate fillers or natural fibres) is a very versatile approach. Depending on the filler characteristics, composition and interface properties, different types of material can be obtained.

Composites can be classified in different categories according to the structure or geometry of the reinforcement:

- **Particulate composites:** in which there are particles distributed or embedded in a matrix body. The particles can be in flakes or in powder form.
- **Fibrous composites:** in which the fibres are embedded in the matrix material. The composite can be considered a discontinuous fibre or short fibre composite if its properties vary with fibre length. The aspect ratio of the fiber (that is the ratio between the fiber length and its diameter) influences the composites class and properties (for examples composites having fiber aspect ratio lower than 10 can be considered ultra-short fiber composites).
- **Laminar composites:** made of layers of materials held together by matrix. Sandwich structures is an example of this category.

Different natural fillers have been used for PLA and other bio-based polyesters, aiming at the improvement of the thermomechanical behaviour as well as the technological performances, i.e. barrier properties. Natural fillers are fibres (e.g. cellulose, chitin) as well as montmorillonites (Table 4) and hydrotalcites, which are inorganic mineral compounds made of phyllosilicates intercalated with cations or anions. Generally speaking, the addition of a hard, rigid filler usually increases polymer stiffness, and results in an increased elastic modulus. Natural fillers usually increase crystallinity, also contributing to increase the stiffness of the polymer matrix. In addition, especially in the case of light fibres, the addition of the natural filler decreases the density of the final polymer-based material, resulting in lighter but strong and resistant manufacts. The best performances are achieved when the compatibility between the filler and the matrix is high, i.e. either making the polymer matrix hydrophilic or coating the fibres with hydrophobic surfaces. In this case, the dispersion of the filler is achieved at the molecular level (exfoliation), thus maximizing polymer-filler interaction surface. When at least one of the 3 dimensions of the filler is nanometric, a nanocomposite occurs (Figure 5).

Table 4. Suppliers of bentonite

Product	fillosilicate	producer	country
Bentonite	montmorillonite	Laviosa	Italy
Bentonite	montmorillonite	Long Range Europe	U.K.
Bentonite	montmorillonite	Pfizer Pharma GmbH	Germany

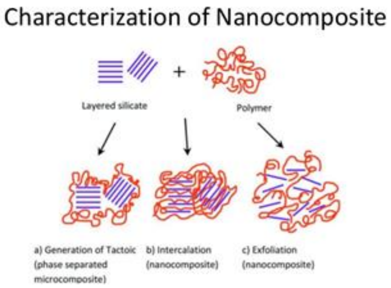

Figure 5. Characterization of nanocomposites with inorganic platelets.

An interesting group of biocomposites is characterized by biopolymers reinforced with natural fibers. The use of natural fibres is being driven not only by environmental reasons but also economical ones. In fact, natural fibre-reinforced biocomposites are primarily used as low-cost materials.[22]

Furthermore, due to the growing amount of wastes generated, there is a growing consideration in the utilization of wastes for the production of sustainable composite materials.[23] Natural fibres are renewable, biodegradable and they are less abrasive to tooling. In particular, lignocellulosic fibers have been investigated as possible promising solutions for the substitution of synthetic fibers in polymer composites. Especially for those applications (such as packaging and agriculture sectors) where biodegradability offers clear advantages for customers and the environment, it is expected that the demand of biocomposites (constituted by a biopolymer coupled with natural fibers) will grow up.[24]

Different types and examples of natural fibers can be classified according to their origin (Figure 6). Generally, plant or vegetable fibers are used to reinforce thermoplastic polymers. The introduction of natural fibers lead to a composite material possessing high strength and modulus.

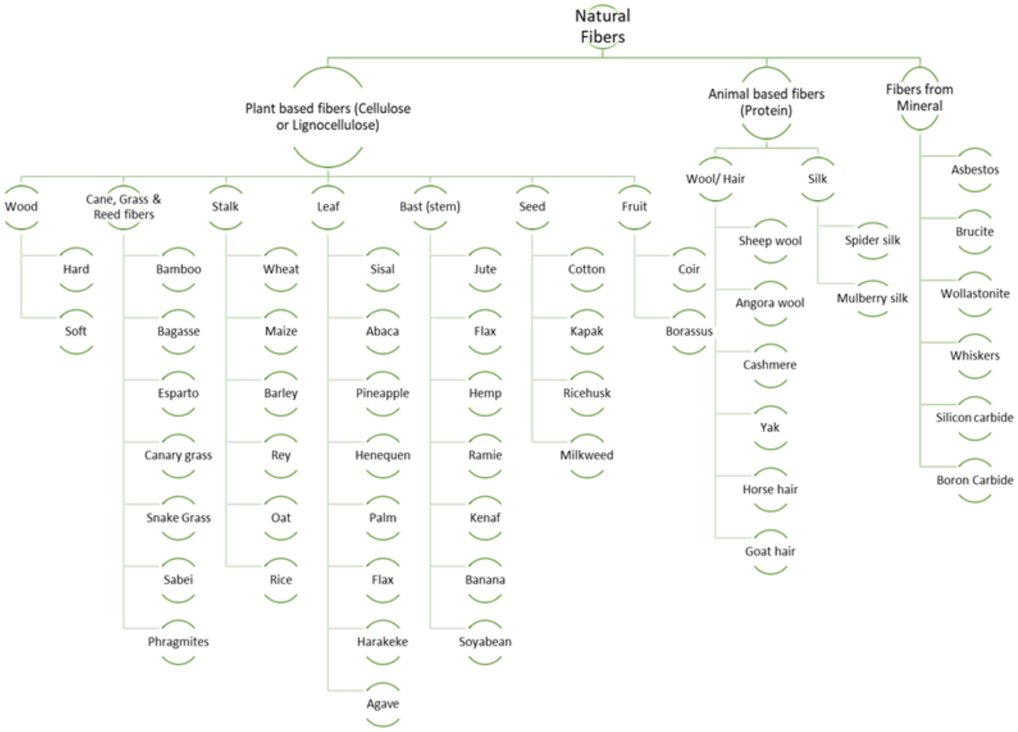

Figure 6. Classification of natural fibres according to their origin.

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[22] Gurunathan, T.; Mohanty, S.; Nayak, S.K. A review of the recent developments in biocomposites based on natural fibres and their application perspectives Composites: Part A A review of the recent developments in biocomposites based on natural fibres and their application perspectives, 77, (2015), 1 – 25.

[23] Mohammadhosseini, H.; Tahir, M. Production of sustainable green concrete composites comprising industrial waste carpet fibres, in: Muthu, S.S. (Ed.), Green Compos. Sustain. Raw Mater., Springer Singapore, Singapore, 2019: pp. 25 – 52.

[24] (a) Aliotta, L.; Gigante, V.; Coltelli, M.B.; Cinelli, P.; Lazzeri, A.; Seggiani, M. Thermo-mechanical properties of PLA / short flax fiber biocomposites, *Appl. Sci.*, **2019**, *9*, 3797 – 3812. (b) Aliotta, L.; Gigante, V.; Coltelli, M.B.; Cinelli, P.; Lazzeri, A. Evaluation of mechanical and interfacial properties of bio-composites based on poly(lactic acid) with natural cellulose fibers. *Int. J. Mol. Sci.*, **2019**, *20*, 960 – 974.

Nevertheless, the addition of natural fibers needs of special attention in order to obtain biocomposites with good mechanical properties. In fact, differently and compared to synthetic composites, the composites containing natural fibers show some drawbacks such as: lower mechanical properties, high moisture absorption and lower durability. Furthermore, natural fibers contain a large amount of cellulose, hemicellulose, lignin and pectin that tend to be active polar hydrophilic material while polymeric matrices, being not polar, show hydrophobic properties. Consequently, generally there is a weak interfacial adhesion between natural fibers and polymeric matrices.[25]

Different approaches have been investigated to improve the interfacial compatibility and bond strength as the use of surface modification techniques. Different chemical treatments that use sodium hydroxide, peroxides, organic, and inorganic acids, silane, anhydrides, and acrylic monomers have been proposed in order to eliminate the non-cellulosic part (in cellulosic fibers). At the same time, the addition of functional group would provide a better chemical bonding between the fibers and the matrix improving their compatibility.[26] Surface properties of the fibers can be improved by de-lignifications, bleaching, de-waxing (de-fatting), acetylation, and chemical grafting, cyano-ethylation for properties enhancement. However, depending on the feedstock from which the natural fibers derive, their mechanical properties vary within a wide range of values, as it can be observed in Table 5 in which the main mechanical properties of common natural fibers studied in literature are reported.[27]

Table 5. Mechanical properties of common natural fibers

Fibers	Tensile Strength (MPa)	Elongation at break (%)	Young's Modulus (GPa)
Hemp	300 - 800	1.3 - 1.5	30 - 60
Flax	345 - 1500	2.7 - 3.2	50 - 70
Sisal	468 - 700	3 - 7	9.4 - 22
Ramie	400 - 938	1.2 – 3.8	61.4 - 128
Kenaf	295 - 1191	1.6 - 5.7	10.9 - 53
Jute	393 - 800	1.16 – 1.5	13 – 26.5
Spider Silk	1300 - 2000	28 - 30	30
Coir	131 - 220	15 - 40	4 - 6
Cotton	287 - 800	7 - 8	5.5 – 12.6
Henequen	430 - 570	3.7 – 5.9	10.1 – 16.3
Bamboo	140 - 230	2.5 – 3.7	11 - 17
Wool	50 - 315	13.5 - 35	2.3 - 5
Regenerated cellulose	556 - 790	7.1 – 10.3	23.4 – 30.5

Furthermore, many fibers produced from scraps of industrial or agricultural wastes are not yet commercially available. The lack of many of these fibers to be commercially available severely limits their

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[25] Jawaid, M.; Abdul Khalil, H.P.S. Cellulosic/synthetic fibre reinforced polymer hybrid composites: A review. *Carbohydr. Polym.*, **2011**, *86*, 1 – 18.

[26] Sawpan, M.A.; Pickering, K.L.; Fernyhough, A. Effect of fibre treatments on interfacial shear strength of hemp fibre reinforced polylactide and unsaturated polyester composites. *Compos. Part A Appl. Sci. Manuf*. **2011**, *42*, 1189 – 1196.

[27] (a) Lalit, R.; Mayank, P.; Ankur, K. Natural fibers and biopolymers characterization: A future potential composite material. *Stroj. Cas.*, **2018**, *68*, 33 – 50. (b) Graupner, N.; Herrmann, A.S.; Müssig, J.Natural and man-made cellulose fibre-reinforced poly(lactic acid) (PLA) composites: An overview about mechanical characteristics and application areas. *Compos. Part A Appl. Sci. Manuf.*, **2009**, *40*, 810 – 821. (c) Adusumali, R.B.; Reifferscheid, M.; Weber, H.; Roeder, T.; Sixta, H.; Gindl, W. Mechanical properties of regenerated cellulose fibres for composites. *Macromol. Symp.*, **2006**, *244*, 119 – 125.

utilization. In the following table (Table 6), some examples of common and commercially available natural fibers are reported.[28]

Table 6. Commercially available natural fibers

Fibers	Supplier	Country
Jute	JB Plant Fibres Ltd	UK
Kenaf	Merck Chemicals	Germany
	National Kenaf Tobacco Board	Malaysia
	Kenaf Industries Ltd.	USA
Flax	Zhengda chemical	China
Bamboo	Kyoto Municipal Industrial Research Institute	Japan
Retted hemp bast	Hemcore	UK
Wool from waste	Hengyuanxiang (Group) Co., Ltd	Shanghai, China
Ramie Fabrics	Hunan Dongting Maye Company	China
Sheath of the banana plant	Taiwan Banana Research Institute	China
Sisal	Dongfang Sisal Group Co. Ltd.	China
Brown coir	Tianjin Jia Add Green Products Technology Co., Ltd.	Tianjin, China
Cotton	Jiangsu Yongxing Absorbent Cotton Co., Ltd	China

Among all the cereals cultivated in Europe, i.e. barney, wheat, corn, oat, and rice, wheat, a type of grass plant, is second only to rice as the main human food crop. Commercially, *Triticum aestivum vulgare* and *Triticum turgidum durum* (hard wheat, mainly used in pasta products) are of most importance.[29] The wheat grain or 'caryopsis', which is harvested for human nutrition, is composed of a number of different tissues[30] (Figure 7): the germ (or embryo); the endosperm, which is packed with starch grains to provide energy for germination; the thick cell-walled aleurone layer, encasing the endosperm; and the pericarp. The bran fractions consist of the pericarp, testa, and hyaline and aleurone layers.

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[28] (a) Lee, S.H.; Ohkita, T.; Kitagawa, K. Eco-composite from poly(lactic acid) and bamboo fiber. *Holzforschung*, **2004**, *58*, 529 – 536. (b) Shih, Y.F.; Huang, C.C. Polylactic acid (PLA)/banana fiber (BF) biodegradable green composites. *7th Asian-Australasian Conf. Compos. Mater.*, **2010**, 1325 – 1328. (c) Qian, J.; Yu, M.M.; Ge, Z.; Xu, M.J.; Zhang, H.H.; Yang, G.S.; Shao, H.L. Preparation and properties of cotton fiber/poly(lactic acid) composites. *Mater. Sci. Forum.*, **2014**, *789*, 100 – 105. (d) Xia, X.; Liu, W.; Zhou, L.; Liu, H.; He, S.; Zhu, C. Study on flax fiber toughened poly(lactic acid) composites. *J. Appl. Polym. Sci.*, **2015**, *132*, 1 – 10. (e) Ramesh, M. Kenaf (Hibiscus cannabinus L.) fibre based bio-materials: A review on processing and properties. *Prog. Mater. Sci.*, **2016**, *78 – 79*, 1 – 92. (f) Wang, C.; Ren, Z.; Li, S.; Yi, X. Effect of ramie fabric chemical treatments on the physical properties of thermoset polylactic acid (PLA) composites. *Aerospace*, **2018**, *5*, 93 – 105. (g) Sawpan, M.A.; Pickering, K.L; Fernyhough, A. Characterisation of hemp fibre reinforced Poly(Lactic Acid) composites. *Int. J. Mater. Prod. Technol.*, **2009**, *36*, 229 – 240. (h) Li, Z.; Zhou, X.; Pei, C. Effect of sisal fiber surface treatment on properties of sisal fiber reinforced polylactide composites. *Int. J. Polym. Sci.*, **2011**, *2011*, 1 – 7. (i) Tawiah, B.; Yu, B.; Ullah, S.; Wei, R.; Yuen, R.K.K.; Xin, J.H.; Fei, B. Flame retardant poly(Lactic acid) biocomposites reinforced by recycled wool fibers - thermal and mechanical properties. *Express Polym. Lett.*, **2019**, *13*, 697 – 712.

[29] Macrae, R.; Robinson, R.K.; Sadler, M.J. 1993. Encyclopaedia of food science, food technology and nutrition. London: Academic Press.

[30] Stevenson, L.; Phillips, F.; O'sullivan, K.; Walton, J. Wheat bran: its composition and benefits to health, a European perspective. *Int. J. of Food Sci. and Nutrition*, **2012**, *63*, 1001 – 1013.

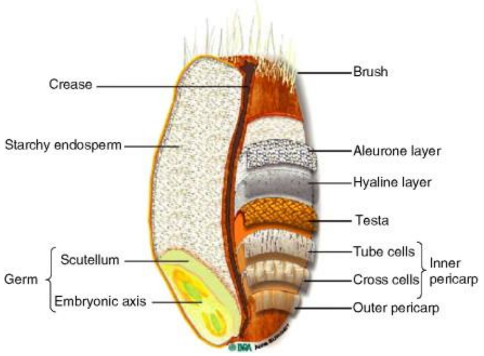
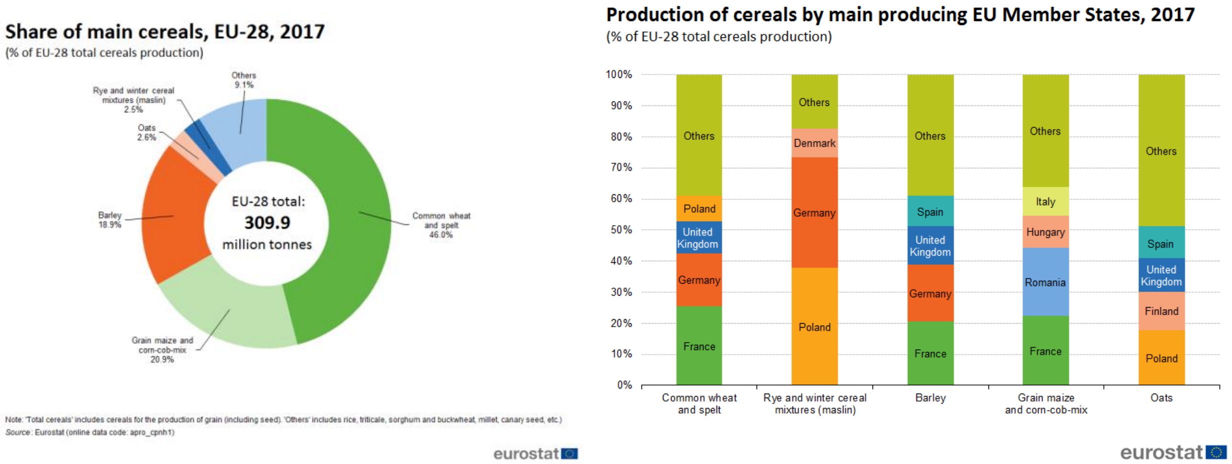


Figure 7. structure of grain caryopsis.

By weight, the wheat caryopsis is composed of an outer branny husk (14 – 16 % of the grain), the germ or embryo (2 – 3 %), and the central endosperm (mainly starch: 81 – 84 %).[31] Conventional milling of wheat grains is based on separating the endosperm (which produces white flour when milled) from the bran layers and embryo. The aleurone cells, along with the other bran layers and the embryo, are removed to form the bran fraction.

Grain husk, or bran, a by-product of the production of flour, is an example of natural waste that nowadays is not managed efficiently. Its cost is currently at 105 Euro/ton., but it is quite variable. The harvested production of cereals (including rice) in the European Union (EU) was 310 million tonnes in 2017, about 12 % of global production. This represented an increase of 2.7 % (8.2 million tonnes) compared with 2016, despite drought conditions in many areas of central and southern Europe and a reduction in cultivated areas of 1.6 million hectares. In spite of the upturn, the EU's harvested production of cereals in 2017 remained below the 2014 peak of 333 million tonnes. Common wheat and spelt represented 46 % of all cereal grains harvested in the EU in 2017. As a share, this was followed by grain maize and corn-cob-mix (21 %) and barley (19 %). Oats, rye and other cereals accounted for the remaining 14 % of cereal production (Figure 8).


Share of main cereals, EU-28, 2017

(% of EU-28 total cereals production)

Note: 'Total cereals' includes cereals for the production of grain (including seed). 'Others' includes rice, triticale, sorghum and buckwheat, millet, canary seed, etc.)
Source: Eurostat (online data code: apro_cpnh1)

eurostat

Production of cereals by main producing EU Member States, 2017

(% of EU-28 total cereals production)

eurostat

Figure 8. data about production of cereals in Europe: (a) share of main cereals; (b) production considering main producing EUmembers (https://ec.europa.eu/eurostat/web/products-eurostat-news/-/DDN-20190311-1).

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[31] Pomeranz Y. 1988. Chemical composition of kernel structures. In: Pomeranz Y, editor. Wheat: chemistry and technology. 3rd ed, Berlin: Springer. pp 99.

Considering that bran represents about 15 % of cereals, the annual production of bran is at about 46,5 Million of tons/year. Hence there is a very high availability of bran in Europe, that can significantly feed industrial chains.

Recently, there have been many scientific works on the use of different natural wastes as components in the production of new composite materials and polymers, in the perspective of the promotion of sustainable economic development and issues related to ecological and environmental protection.[32] However, wheat husk and bran in general present many drawbacks with respect to other natural fillers for polymer composites production: indeed, bran is not actually an officially commercially available product, but can be purchased in large quantities as a residue by farmers of intensive agriculture. This means that, even if availability is not a problem, composition in terms of cellulose, mixed linked ⍰-D-glucans, lignin and starch content may change from batch to batch, depending on the season, rain and other not controllable variabilities. Moreover, morphology of the bran is always highly variable, leading to a product having low aspect ratio compared to other natural products, such as bamboo or cannabis sativa fibres, which are used even in construction applications, due to their relevant mechanical properties.

Conclusions

Deliverable D1.2 reports a comprehensive study on the available bio-based materials that can potentially be employed in BIOnTop. Thus, commercially available grades of PLA, diacids for copolymerization, and bio-based additives and fillers are listed. The information reported in D1.2 makes possible the selection of the final materials and their specifications. The final selection based on this document will be reported in the upcoming deliverable D1.3.

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[32] Majewski, Ł.; Cunha, A.G. Evaluation of suitability of wheat bran as a natural filler in polymer processing plastic & wheat bran. *BioResources*, **2018**, *13*, 7037 – 7052.