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Development and Life Cycle Assessment of Polyester Binders Containing 2,5-Furandicarboxylic Acid and Their Polyurethane Coatings

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Abstract

This work presents a new polyester binder based on 2,5-furandicarboxylic acid (FDCA) as precursors of polyurethane (PU) coatings. The new 100% bio-based structure is composed of four different monomers such as glycerine (Gly), 1,3-propanediol (1,3-PD), 2,5-furandicarboxylic acid (FDCA) and succinic acid (SA). The corresponding PU coating was obtained by crosslinking with a conventional polyisocyanate (Vestanat 1890/100). Evaluation of technological performances is present and benchmarked against partially bio-based (75% renewable carbon) polyester binder and fossil-based polyester binder, already developed in one of our previous work. The study showed a stiffer PU coating and a more hydrophilic character leading to better adhesion where a possible potential application may be interesting as an intermediate layer/primer in the field of metal coating (coil coating, automotive). Afterwards, the evaluation of the total impact of greenhouse gas emissions (GHG), the total non-renewable energy use (NREU) by the Life Cycle Assessment (LCA) for the new polyester binder are included on a cradle-to-gate approach, and considering an FDCA production process starting from sugar beet (primary data). The results showed a very noteworthy reduction in terms of GHG emissions (−36 and −79%) and a noticeable reduction impact in terms of NREU (−38 and −60%) compared to 75% bio-based and fossil-based polyester binders respectively. Moreover, a sensitivity analysis regarding sugar production from beet cultivation was developed through different LCA calculation methodologies. Those methodologies showed a not very significant difference between them.

Graphical Abstract
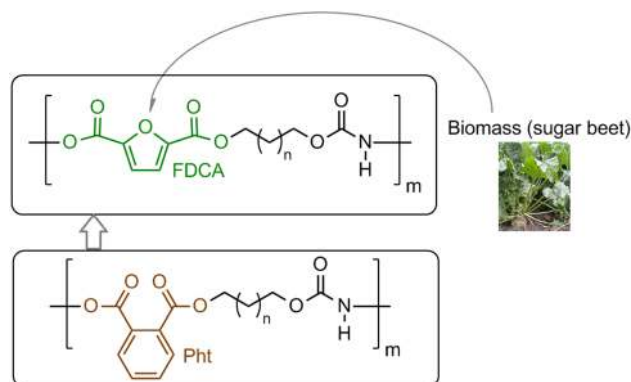
Extended author information available on the last page of the article

Introduction

Polyurethanes (PUs) are one of the most used coating materials in many manufacturing sectors (automotive, furniture, heavy duty) due to their excellent durability and mechanical properties [1]. PUs are actually the sixth most used polymer on a global scale with an annual production of over 12 million tons [2]. One of the emerging topics in modern PU technology is the exploitation of monomers and macromers from renewable resources to improve the environmental sustainability while preserving the excellent technical performances [3, 4]. In fact, many works on bio-based PU coatings have appeared in literature for different applications [5, 6]. PU coatings are obtained by the stoichiometrically balanced mixture and crosslinking of polyols (polyether and frequently polyester oligomers) with polyisocyanates. By a careful selection of different polyols and isocyanates, a variety of PUs with specific properties can be developed for a broad range of industrial applications like foams, paints, thermoplastics, fibers and adhesives [7–9].

Polyester polyols are the largest fraction in the composition of PU coating material. They are made from aliphatic as well as aromatic diacids and hydroxy functional monomers [10]. Within aromatic acids, 2,5-furandicarboxylic acid (FDCA) is a relatively "new" bio-based building block with a unique structure that is attracting great interest. Actually, it is the only substance containing aromatics among the top 12 bio-derived chemicals listed by the U.S. Department of Energy (DOE) in 2004 and updated in 2010 [11]. Although FDCA could be produced from cellulose or hemicellulose, the production of furan derivatives from sugars, synthesized chemically from 5-hydroxymethylfurfural (HMF), has recently become a promising route in green chemistry and in catalysis studies [12]. In recent years, polyester polymers and copolymers based on FDCA have received special attention in many aspects regarding monomer synthesis, polymerization reactions, application [13, 14] and characterization [15–17]. FDCA was mainly proposed as a green alternative to petrochemical-derived terephthalic acid to produce thermoplastic polyesters [18, 19]. A recent paper [20] presented an overview of the developments and future prospects on bio-based polyesters from FDCA and other renewable resources. They can be used as biomaterials [21] with competitive properties [22] and potential applications as thermoplastics as well as elastomers [23].

In spite of the high industrial interest, only a few papers are available in the open literature [24, 25] concerning the evaluation of environmental impacts related to FDCA production. The work by Isola et al. [25] reported the application of the LCA model for the laboratory-scale production from the conversion of fructose to HMF, FDCA monomer, the corresponding polymer, its recycling and the total impacts are observed individually. However, the laboratory-scale evaluation of consumables led to an overall high total impact in many different categories, such as the climate change. Eerhart's work was focused on the LCA of the production of polyethylene furandicarboxylate (PEF) using furanics as intermediates, starting from corn based fructose, and evaluating the non-renewable energy use (NREU) and greenhouse gas (GHG) impacts. This LCA study has become, so far, the only available one at industrial scale where the different steps for FDCA production are considered.

Most of the studies concerning FDCA-based polyesters are about thermoplastics, but there is a lack of information in the literature about polyester copolymers based on FDCA as precursors for PU coatings. Due to this, the main objective of this work is to present a new class of polyester binders based on FDCA suitable as precursors of PU coating materials. The new 100% bio-based structure was re-designed and obtained through the selection and copolymerization of four different monomers, all available from modern biorefinery downstreams such as glycerine (Gly), 1,3-propanediol (1,3-PD), 2,5-furandicarboxylic acid (FDCA) and succinic acid (SA). The corresponding PU coatings were obtained and their technological performances were benchmarked against partially bio-based (75% renewable carbon) and fossil-based polyester binders, already developed by our group and described in a previous work [26]. Moreover, the evaluation of the total impact of greenhouse gas emissions (GHG), the total non-renewable energy use (NREU) by the Life Cycle Assessment (LCA) are included on the basis of a cradle-to-gate approach separating the contributions due to the monomer mixture composition and those related to the copolymerization process, and considering a FDCA production process starting from sugar beet (primary data). Specifically, a finer analysis of the impact of marine eutrophication and freshwater eutrophication is allowed, providing relevant information about the environmental implication of the production of a chemical derived by biomass (sugar beet), as the case of the present study.

Experimental Section

Materials

All materials used in this study are commercially available. The conventional polyisocyanate used for crosslinking,

called commercially Vestanat 1890/100, was supplied by Evonik Industries. It was a cycloaliphatic polyisocyanate based on isophorone diisocyanate (IPDI). 1,2-propanediol (1,2-PD), 1,3-propanediol (1,3-PD), succinic acid (SA), adipic acid (AA), phthalic anhydride (Pht), glycerine (Gly) used for the synthesis of the polyesters and the solvents needed to reduce the viscosity such as butyl acetate (BA) and propylene carbonate (PCC) were all purchased from Sigma–Aldrich. FDCA monomer was provided by the Sinochem Jiangsu Co., Ltd. (Middle, Nanjing, China).

Preparation of Sustainable PU Coating from 100% Bio-based PE Binder

The PU coating indicated as PU1_100% was obtained by crosslinking with a conventional polyisocyanate (IPDI) a model, 100%-biobased 4-monomer polyester binder (named PE_100% in the following) made by a 4-monomer copolymerization. The synthesis PE_100% was made through a bulk polycondensation process. The monomers reported in Table 1 were charged in a three-necked glass flask and polymerization was accomplished with a progressive increase of high temperature from 150 to 210 °C, under mechanical stirring at 60 rpm and a dry nitrogen flow to remove water formed as by-product. The progress of the reaction was then checked by end group titration which monitored the residual acidity of polyesters, and the polymerization was stopped when the acid number was < 10 mgKOH/g. Production and characterization of 100%-biobased PE binder, partially biobased PE_75% binder and fossilbased PE_Fossil binder are reported in this study. Characterization consisted in thermal analysis by differential scanning calorimetry (DSC) and molecular weight measurement by gel permeation chromatography (GPC). The coatings were obtained by formulation of the selected polyester and the appropriate amount of isocyanate crosslinker in a 30%

solid solution in propylene carbonate, together with a OH/NCO stoichiometric ratio = 1.03; the catalyst 1,4-Diazabicyclo [2.2.2] octane (DABCO) was added in amount of 0.5% w/w. The final PU1 coating was applied onto glass and aluminium panels and cured in an oven at 100 °C for 1 h, obtaining a dry film thickness of 20–30 mm. The extent of reaction upon crosslinking was checked by monitoring the progressive disappearance of the NCO band through IR spectroscopy (stretching band at 2260 cm^{-1}). Results were compared to PU2_75% (from PE_75%) and PU3_Fossil (from PE_Fossil) which were reported in our previous work [26]. For PU2_75% and PU3_Fossil, butyl acetate (BA) was used as dilution solvent. All coatings passed the chemical resistance test after curing (MEK test, > 100 double rubs according to ASTM D4752 [27]) confirming that crosslinking has occurred.

Table 1 shows the composition of the two bio-based polyester binders and the source for the evaluation of their ecoprofiles. The composition and source of the fossil-based polyester binder was reported in our previous work [26], and its structure was formed by glycerine (Gly), 1,2-propanediol (1,2-PD), phthalic anhydride (Pht) and adipic acid (AA). The only difference between the two bio-based materials under consideration (PU1 and PU2) is in the nature of the aromatic acid, with replacement of fossil-based phthalic acid and bio-based FDCA passing from PE_75% / PU2 to PE_100% / PU1systems. The characterization of the PU films consisted in thermal analysis by differential scanning calorimetry (DSC), surface wettability by a static optical contact angle (OCA) against water, adhesion by pull-off tests (ASTM D4541-09), indentation hardness by Buchholtz test (ISO 2815) and surface tension by a static optical contact angle (OCA) against water and diiodomethane. Hydrolytic stability was also tested by exposing the coatings at 60 °C, 100% humidity for a period of 30 days. The stability test was repeated in 3 different samples for each composition. The

Table 1 Relevant information and composition of monomers for the two bio-based polyester binders

| Family | PE_75% Garcia Gonzalez et al. [26] | | | | PE_100% (Present study) | | | |
	Monomers	Bio or fossil based	Source	Composition (%w/w)	Monomers	Bio or fossil based	Source	Composition (%w/w)
Polyols	Glycerine (Gly)	Bio (Palm oil)	Secondary data [28]	7.00	Glycerine (Gly)	Bio (Palm oil)	Secondary data [28]	6.90
Aliphatic diols	1,3-propanediol (1,3-PD)	Bio (Corn sugar)	Secondary data [29]	34.70	1,3-propanediol (1,3-PD)	Bio (Corn sugar)	Secondary data [29]	34.05
Aromatic diacids	Phthalic Anhydride (Pht)	Fossil	Secondary data [30]	37.90	2,5-Furandicarboxylic acid (FDCA)	Bio (Sugar beet)	Present study	38.40
Aliphatic diacids	Succinic acid (SA)	Bio (Corn starch)	Secondary data [31]	20.40	Succinic acid (SA)	Bio (Corn starch)	Secondary data [31]	20.65

samples were periodically monitored through contact angle and indentation hardness tests.

Materials Characterization

Differential Scanning Calorimetry (DSC) analysis

Thermal analysis was performed on PE and PU samples using a DSC (MettlerToledo DSC/823e instrument) at a scan rate of 10 °C min^{-1} under nitrogen flux. The measurements consisted of three runs (heating/cooling/heating) from 25 to 150 °C. The samples measured had a weight of around 10–15 mg.

Optical Contact Angle (OCA)- Surface Wettability

The wettability of the PU surfaces was studied performing contact angle measurements using an optical contact angle system (OCA-15-Plus, Dataphysics, Germany) equipped with a CCD photocamera and with a 500 μL Hamilton syringe to dispense liquid droplets. Measurements were made at room temperature by means of the sessile drop technique with dedicated software (SCA 2.0) determining the contact angle based on the Young Laplace fitting method. The pure water (H2O) was used as probe liquid and the delivered volume was 2 μL with 0.5 μL/s as dispense speed. A minimum of 25 measurements were taken in different regions on the surface of each PU film and results were averaged.

Gel Permeation Chromatography (GPC)

The molecular weight of PE samples was estimated by means of gel permeation chromatography (GPC) using a Waters 510 high-performance liquid chromatography (HPLC) system equipped with a Waters 486 tunable absorbance detector set at $\lambda = 300$ nm, using THF as eluent. The sample (200 μL of PE in THF, 2 mg/mL) was injected into a system of columns connected in series (Ultrastyragel HR, Waters) and the analysis was performed at 30 °C and at a flow rate of 0.5 mL/min. The GPC system was calibrated against polystyrene standards in the 102–104 g/mol molecular weight range.

Pull-Off Adhesion Testing

The adhesive properties of the resulting PU materials on different substrates (glass and aluminium chromed) were evaluated with a PosiTest AT-M Manual adhesion pull-off tester (DeFelsko, ASTM D4541-09 [32]) by measuring the pulling force needed to detach a 20 mm-diameter aluminium dolly adhered to the films by means of epoxy adhesive (Araldite

2011, curing cycle: 50 °C, 24 h). 3 determinations of each sample were assessed.

Buchholz Indentation test—Hardness Analysis

The indentation resistance (hardness) of the corresponding PU coatings were evaluated by Indentation Hardness Tester acc. to Buchholz, Model 263 (ISO 2815 [33]). A metal block with testing force between a range of 4.90 N and 4.95 N (equivalent to 500 to 505 g) was applied on each coating surface for 30 s and length (l) of the resulting indentation was measured using a microscope. The indentation resistance ($\acute{\alpha}_B$) values were obtained from the indentation length ($\acute{\alpha}_B = 100/l$, where l is in mm).

Surface Characterization

Surface tension on the corresponding coatings was evaluated by performing contact angle measurements. The procedure was followed using water (H_2O) and diiodomethane (CH_2Cl_2) (Sigma–Aldrich) to compute surface tension. The surface energies and its polar and dispersive components were estimated by Wu's harmonic-mean method [34].

Life Cycle Assessment (LCA) on Polyester Binders

System Boundary

Figure 1 shows the system boundary of the three polyester binders according to a cradle-to-factory gate view. As for the FDCA monomer, the simplified flow diagram for its production is shown in Fig. 2. The FDCA production system is divided into five major steps: sugar beet cultivation; transport of beet to the plant and the sugar production; conversion of fructose; conversion of 5-HMF and finally oxidation of 5-HMF to the FDCA. Transport of the raw materials and the production of the farm equipment, such as beet harvesters and tractors used in the sugar production step, and the intermediate transport steps from sugar production to FDCA production, were outside the system boundaries and not considered. The multiple operational steps along with the description for the sugar production from beet cultivation are shown in Supporting Information.

Methodology

This study focuses on the 'Cumulative Energy Demand' [35] (v1.09) method which covers the impact category of non-renewable energy use (NREU) including fossil and nuclear energy and the 'Greenhouse Gas Protocol (GGP)' (v1.01) method which covers the impact category of GHG emissions. The GGP method is chosen to perform a Carbon
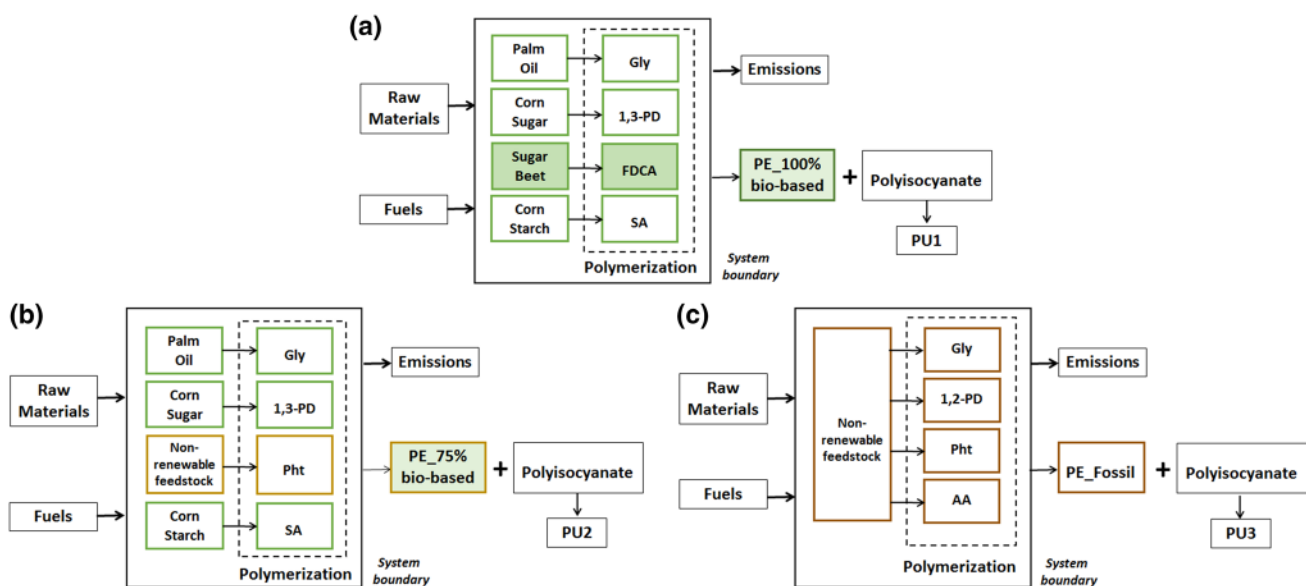
Fig. 1 The system boundary of the different polyesters: **a** PE_100%, **b** PE_75%, and **c** PE_Fossil. Green boxes represent the monomers from renewable resources for the bio-based polyester binders
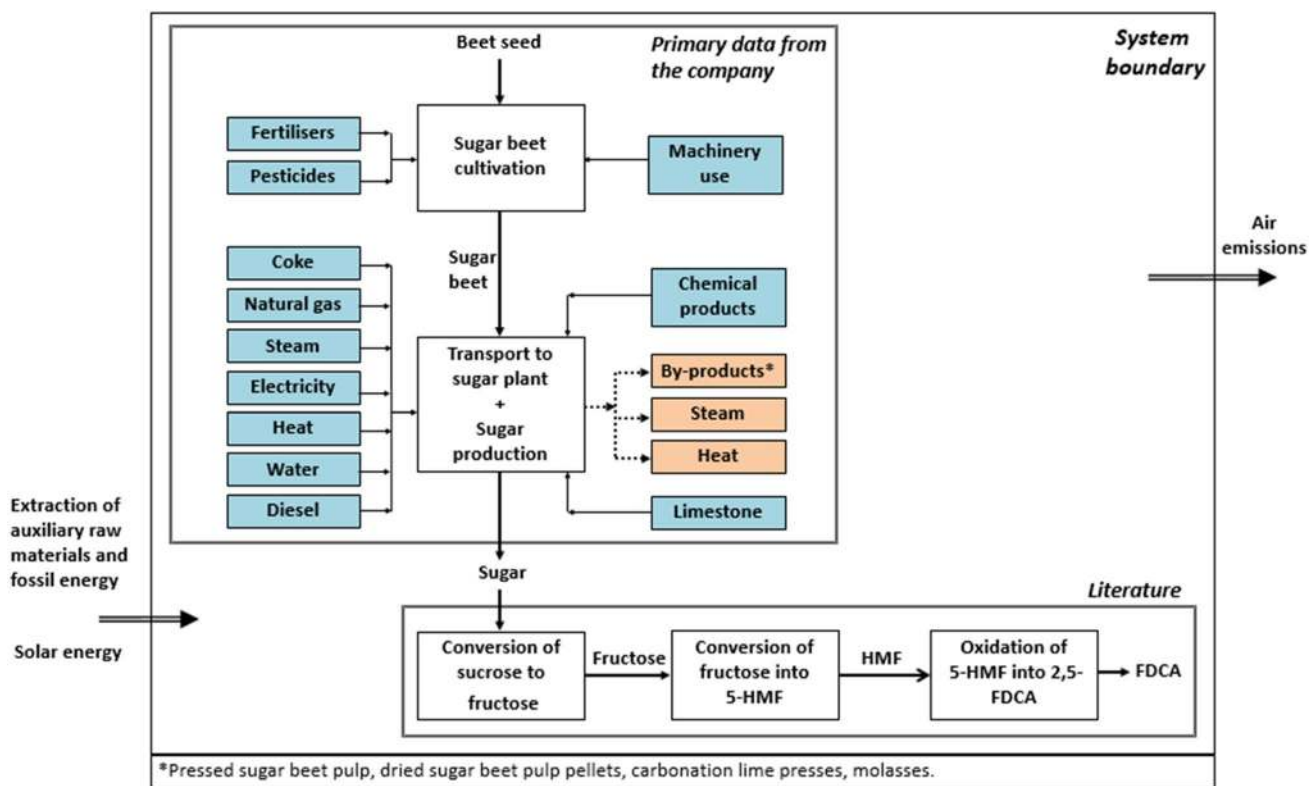

Fig. 2 The system boundary of the FDCA production from sugar beet cultivation. Blue and orange boxes represent all the relevant inputs and outputs included in sugar beet cultivation and sugar production respectively

Footprint of the different alternatives analysed. This method leads to measure the amount of greenhouse gases (in kg CO_2eq) emitted to the atmosphere contributing to global climate change, which includes emissions from fossil and biogenic carbon sources, emissions caused by land use change and carbon uptake by plants over a 100-year time

horizon. To calculate carbon dioxide equivalents (CO_{2eq}) of all non-CO_2 gases (CH_4, N_2O, SF_6, HFCs and CFCs) the 100-year IPCC global warming potentials (GWP) are used in (IPCC [36]). The 100-year GWP is a metric used to describe the time-integrated radiative characteristics of well mixed greenhouse gases over a 100-year time horizon. For the sugar production from beet cultivation, the 'Recipe Midpoint (H)' [37] (v1.12), method based on the GWP100 (100-year timeframe), was also used to analyse the impact categories of marine eutrophication and freshwater eutrophication, as they are relevant in the production of a substance derived from a cultivated biomass feedstock, as it is the case of this study (sugar beet) thanks to the primary data information. The latter impact categories could not be used in all the study, as this information was not found in the literature for the other steps [26]. The characterization factors for each emission used are shown in Supporting Information. The analysis was developed following the LCA methodology, which is standardised in the ISO 14040-14044 series by the International Organization of Standardization (ISO 14040-14044 [38, 39]). Sensitivity analysis was developed on sugar production from sugar beet cultivation as primary data were added for PE_100% production compared to the other polyesters (PE_75% and PE_Fossil). This analysis was tested through different LCA calculation allocations such as economic and energy. The functional unit is one kg of 100% biobased polyester binder, the basis to compare partial biobased polyester versus fossil-based polyester.

Data Used in the Study

As it is mentioned before in Table 1 and in the previous work, the monomers (except FDCA) were selected according to their primary data availability in the Ecoinvent database version 3.2, and in the open literature for the study of life cycle on polyesters. As for FDCA production, in the

two first steps (beet cultivation and sugar production), the analysis was performed with the most recent, primary and detailed data provided by Nordic Sugar A/S, Örtofta Sugar Factory, Sweden during the campaign of 2015. Emissions to air derived from crop management were calculated by the IPCC method (2006) (IPCC [40]) to obtain the atmospheric emissions that are the precursors of climate change (carbon dioxide, nitrous oxide, methane). In the development of this calculation of emissions, some secondary data obtained from the literature [41] were used, as it is the case of the amount of nitrogen in animal manure, which was applied on the soil for sugar beet cultivation. Emissions to water derived from crop management were based on literature data including regional specific climate and soil conditions and some assumptions were applied. The gross nitrogen leaching was estimated to be expressed as 30 kg N per hectare per year [42] and the gross phosphorous leaching was estimated to be expressed as 0.5 kg P per hectare per year [42]. The data used in the FDCA production's last 3 steps (see Fig. 2) were secondary obtained by Eerhart's work [24]. Some assumptions were needed in the conversion of fructose step for the impact category of GHG emissions. The energy that was considered was natural gas (same energy that was used in the sugar production step). Finally, all data were incorporated into the SimaPro LCA software, and into the Ecoinvent database version 3.2 with an attributional system model that was used as a background source in some processes for FDCA production and the polyester binders. Whenever it was possible, models based on European technology (RER) were used within the system; however, some processes had models based only on the rest of the world's technology (ROW). In this case, they were used as a substitute to Europe's based models. The LCA limitations of each impact category for the PE_100% including the FDCA are summarized in Table 2. Inventory analysis for the PE_100% according to the composition shown in Table 3 and the relevant data for the FDCA

Table 2 The LCA limitations of each impact category for all polyesters and FDCA

	Impact categories	LCA limitations
PE_100%	GHG emissions NREU	Secondary data information in literature
PE_75%	GHG emissions NREU	Secondary data information in literature
PE_Fossil	GHG emissions NREU	Secondary data information in literature
FDCA	GHG emissions NREU	Secondary data information in literature
SUGAR PRODUCTION FROM SUGAR BEET CULTIVATION	GHG emissions (supporting information) NREU (supporting information) Marine eutrophication Freshwater eutrophication	Primary data information (our study)

Table 3 Inventory analysis for 1 kg of PE_100% production. The data not shown in the table are from Ecoinvent. Energy refers the non-renewable energy use in each monomer

Polyester binder	Input			Output		
PE_100%	Materials		Unit	Materials		Unit
	Gly Bio	0.07	kg	PE	1.00	kg
	1,3-PD	0.34	kg			
	FDCA	0.39	kg			
	SA	0.21	kg			
	Energy			Emissions to air		
	Gly Bio	–		Gly Bio	–	
	1,3-PD	21.80	MJ	1,3-PD	0.74	kg CO$_2$eq
	FDCA	6.14	MJ	FDCA	0.45	kg CO$_2$eq
	SA	6.76	MJ	SA	0.18	kg CO$_2$eq

Table 4 Relevant data on process data for 1 kg of FDCA production from sugar beet cultivation. The inventory analysis for the sugar production is presented in Supporting Information

GHG emissions		
Sugar from beet (calculated)	0.71	kg CO$_2$eq/ kg sugar
Fructose from sugar (assumption)	0.23	kg CO$_2$eq/ kg fructose
FDCA from fructose (literature [24])	0.24	kg CO$_2$eq/ kg FDCA
TOTAL GHG emissions FDCA from sugar beet	1.18	kg CO$_2$eq/ kg FDCA
NREU		
Sugar from beet (calculated)	7.11	MJ/kg sugar
Fructose from sugar (literature [24])	3.90	MJ/kg fructose
FDCA from fructose (literature [24])	5.00	MJ/kg FDCA
TOTAL NREU FDCA from sugar beet	16.0	MJ/kg FDCA

production is also shown in Table 4. The inventory analysis for PE_75% and PE_Fossil is shown in Garcia Gonzalez et al. [26].

Allocation on Sugar Production

Allocation is required in the sugar production step for the obtainment of FDCA; the procedure defined by ISO 14044 is followed. Seven output flows are obtained in the sugar production, which are white sugar, molasses, dried sugar beet pulp (pellets), pressed sugar beet pulp, carbonation lime presses and energy as steam (energy drying) and heat (energy heating) (see Supporting Information for a detailed explanation). Allocation of impacts is a very important methodological issue of LCA practitioners and its definition is 'Partitioning the input or output flows of a process or a product system between the product system under study and one or more other product systems' (ISO 14040-14044) [38, 39]. Two different types of allocations, economic and energy, were studied and their allocation applications for the seven outputs are shown in Table 5. Both allocations were selected by some fundamental reasons: in the energy case, it was assessed due to the fact that sugar mills globally exist, which are bioethanol producers and therefore, an energetic purpose makes it a suitable alternative for this study even though in our specific case it is not produced. In

Table 5 The different percentages of the two applied allocations in sugar production from beet cultivation

Product/by-products	Economic allocation [EA] (%)	Energy allocation [EnA] (%)
White sugar	90.0	81.6
Pellets	4.9	10.9
Pressed sugar beet pulp	0.8	0.4
Molasses	3.5	6.0
Energy drying	0.5	0.7
Energy heating	0.2	0.6

the economic case, it was evaluated by its simplicity and ability to illustrate the properties of complex systems notwithstanding the prices may change over the years and an extended estimated price to a longer period and periodic controls may be needed to enhance its credibility. The data used for energy allocation (EnA) was completely primary. In the case of economic allocation (EA), secondary data were needed for energy outputs obtained from the literature [43–45]. The rest of outputs were primary. EA was assessed in accordance with an estimated average price from the last ten years for sugar and the last five years for by-products that are produced at the factory. EnA was developed according

to the amount of energy as low heating value in sugar and the other by-products. Carbonation lime presses output was excluded in the allocation analysis due to its insignificant value for economic allocation and lack of energy content for energy allocation. The price and energy value for each product were multiplied by the amount in tons of dry matter of each product to obtain the allocation percentage. For the rest of the study, regarding FDCA production, the results from economic allocation were selected as base case and used due to its more effective way to attribute mass and energy outputs to the same unit. Moreover, there were no remarkable differences in the results between both allocations as it is shown in the percentage of sugar in Table 5. The results of sugar production from sugar beet cultivation in terms of GHG emissions, NREU and eutrophication for both allocations are presented in Supporting Information.

Results and Discussion

Solubility Characterization on 100% Bio-based Polyester Binder

In coating technology, a dilution solvent is normally needed in order to reduce the viscosity and to allow a correct film forming mechanism. In our previous work [26], dilution with butyl acetate (BA) was adequate for PE_75% and PE_Fossil formulations. However, more polar solvents are needed for PE_100% containing the FDCA monomer. Among the various solvents tested such as propylene carbonate (PPC), acetonitrile (AN), acetone (AC), tetrahydrofuran (THF) and butyl acetate (BA), PPC was chosen as an optimal solution. Moreover, PPC is considered an environmentally friendly solvent for the development of the sustainable coating [46]. The solubility parameter (δ) of the PCC solvent is 27.2 δ/MPa$^{1/2}$ whereas the BA solvent has a 17.4 δ/MPa$^{1/2}$ of solubility parameter [47]. Those different parameters suggest that PE_100% binder is significantly more polar than the other two resins.

Characterization on 100% Bio-based Polyester Binder

The characterization of the 100% bio-based polyester binders after the copolymerization compared to PE_75% and PE_Fossil is shown in Table 6. The number average molecular weight (Mn) of the polyesters ranged from 1285 to 1775 g/mol and the weight average molecular weight (Mw) from 2578 to 4328 g/mol with a polydispersity index (PDI) between 1.8 and 2.5. All these values are suitable given the nature of polycondensation polymers. The glass-transition temperatures (Tg) of the copolyesters is represented in Table 6. The PE_100% and PE_75% binders showed a

Table 6 PE binder's characterization. Molecular weights (Mn and Mw), polydispersity index (PDI) and acid number (AV) of all PE binders

Samples	Tg (°C)	Mn (g/mol)	Mw (g/mol)	PDI	AV (mg KOH/g)
PE_100%	−8	1775	3138	1.8	14.4
PE_75%	−13	1285	2578	2	12.8
PE_Fossil	6	1726	4328	2.5	6.8

more flexible resin compared to PE_Fossil. According to the substitution of Pht with FDCA, a small difference between bio-based polyesters was observed, being a bit less flexible PE_100% (−8 °C).

Characterization on PU Coating Based on FDCA

Table 7 shows the characterization of the crosslinked PU1 coating compared to PU2 and PU3 properties. Substituting the Pht monomer with FDCA monomer, a stiffer PU1 polymer backbone is formed, with a Tg value of +14 °C compared to +3 °C for PU2. It is due to the fact that the FDCA structure is more symmetric and regular, which makes the interaction between the polymer's chains become stronger and a raising of Tg was shown. When comparing the previous coatings, the fossil-based PU3 one, showed the highest Tg by around +34 °C, which contains 1,2-PD monomer as a chain extender, with methyl side groups, and therefore it shows a less flexible polymer structure. As the indentation behaviour is concerned, the PU1 coating with FDCA-based polyester binder showed the highest hardness between the bio-based coatings (PU1 and PU2), which is in agreement with its higher Tg. However, the 100%fossil-based PU3 coating presented the highest hardness, also in agreement with its Tg. In respect of surface wettability, the contact angle showed a more hydrophilic character for PU1 (80°) whereas PU2 showed a moderately hydrophobic character (88°). The reason may be caused by the more polar character of FDCA with respect to phthalic structures. The adhesion test was evaluated onto glass and chromated aluminium. Both PU coatings applied onto glass and Al chromed substrates showed an excellent adhesion with the highest bonding strength observed on PU1 coating (> 8 MPa), which is in agreement with its hydrophilic character. In Table 8, the surface tension on all PU coatings is reported. PU1 also showed the highest surface tension value by around 43.3 mN/m constituting greater cohesive forces and therefore greater forces of adhesion, which is in agreement with the adhesion test results.

As a last test, the hydrolytic stability test was also assessed and monitored over 30 days of continuous exposure to water at +60 °C. Contact angle and hardness measurements were used to control the quantitative evaluation

**Table 7** Coating characterization

PU coating	Tg (°C)	OCA TEST (°)	Adhesion test (MPA)		Hardness test (αb)
			Glass	Al Chromed	
PU1	14.0	80.0 ± 2.1	> 8	1.3 ± 0.3	83.3 ± 0.1
PU2 [26]	3.0	88.0 ± 3.4	6.4 ± 1.2	1.0 ± 0.2	54.1 ± 0.2
PU3_Fossil [26]	34.0	83.0 ± 1.8	7.3 ± 2.3	1.1 ± 0.4	91.0 ± 0.4

Table 8 Surface tension and its components determined for the PU coating substrates using Wu method calculation

Samples	SFT Polar (mN/m)	SFT Dispersive (mN/m)	SFT total (mN/m)
PU1	9.7	33.6	43.3
PU2	6.7	32.2	38.9
PU3	8.9	32.8	41.7

every 5 days. The results are shown in Fig. 3 and they are expressed as percentage retention of the property over the time. A fast decrease of hardness with a value of 40% less is observed for PU1 after the 5th day monitored by indentation hardness test and it is maintained during the following 30 days. With contact angle test (Fig. 3b), a slight decrease of hydrophobicity is observed in PU1 film during the first 10 days of testing, which are comparable to PU2 and PU3. After the 20th day of testing the hydrophobicity faster decrease reaching 15% less being distanced from PU2 and PU3. This test may confirm the hydrophilic character of the PU1 based on FDCA. A hydrophilic material can absorb water faster swelling the material and therefore, decreasing the hardness.
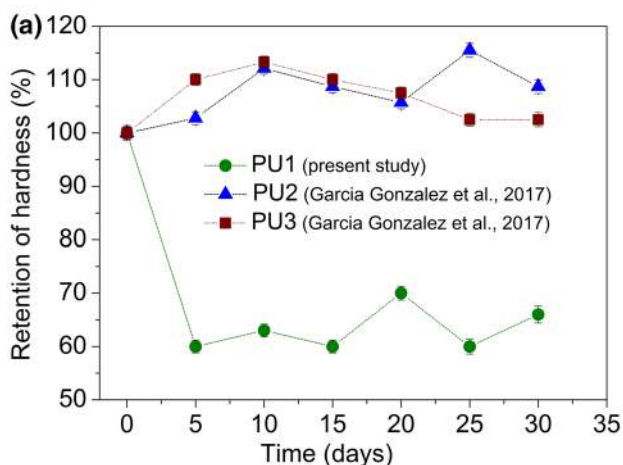
Environmental Impact Assessment

The total NREU and GHG emissions of the three cases were evaluated for 1 kg of polyester and calculated according to the composition of the synthesised polyesters (Table 1). Figure 4a shows the total impact of the GHG emissions with a value of 2.75 kg CO_2eq/kg for PE_75% whereas PE_100% has a lower impact with a value of 1.75 kg CO_2eq/kg. Both show a meaningful reduction compared to PE_Fossil by around 67% and 79% respectively (8.4 kg CO_2eq/kg). The substitution of the phthalic monomer with FDCA into the PE_100%, led to a significant reduction in the latter by around 36% including the polymerization process. As for the total NREU, Fig. 4b shows a value of 96 MJ/kg for PE_Fossil, a 62.5 MJ/kg for PE_75% and a 39 MJ/kg for PE_100% where PE_100% shows a significantly lower impact than PE_75% (-38%) and PE_Fossil (-60%).

Environmental Impacts on Sugar Production

The total phosphate and nitrate contributions of the different steps of the sugar production process from beet cultivation is detailed in this part of the study in Fig. 5. They were evaluated for the reference of 1 ton sugar for both allocations. The phosphorus in phosphate form in the freshwater with a total value of 0.19 kg PO_4^{3-}eq/ton sugar for the economic allocation and 0.18 kg PO_4^{3-}eq/ton sugar for energy
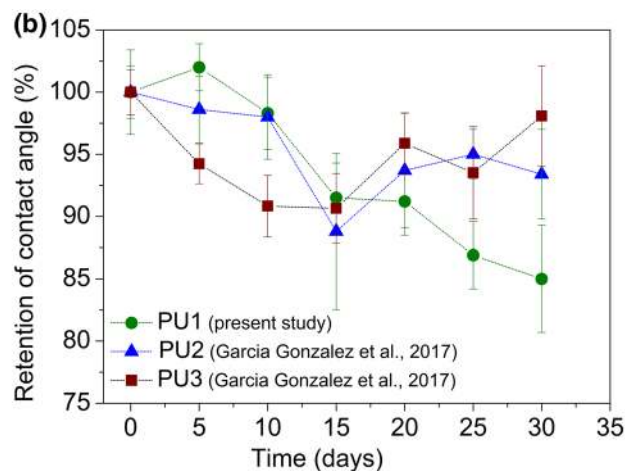
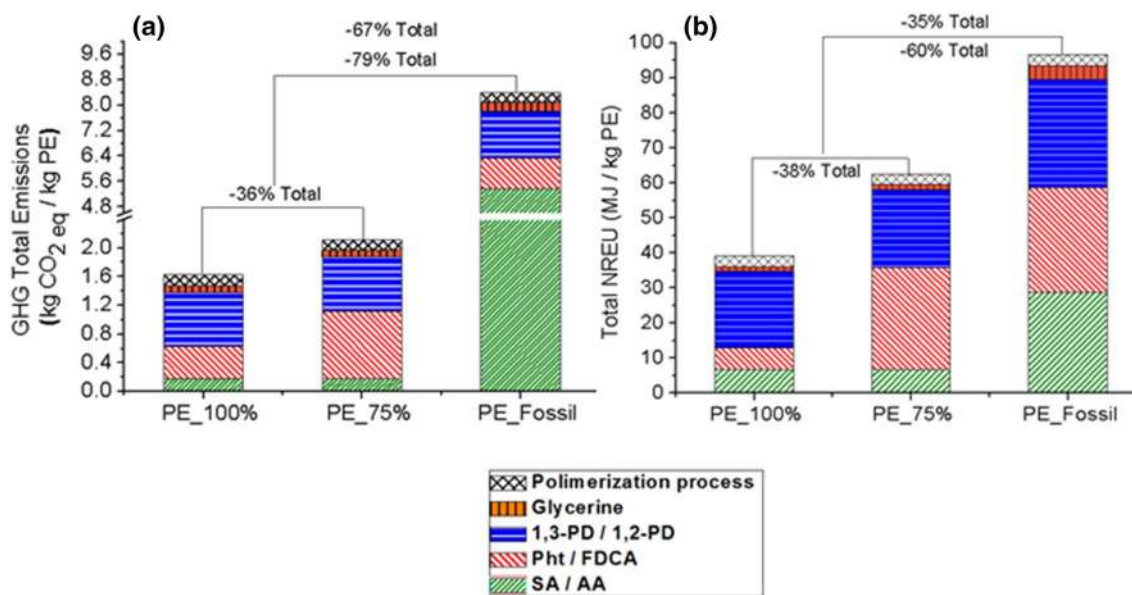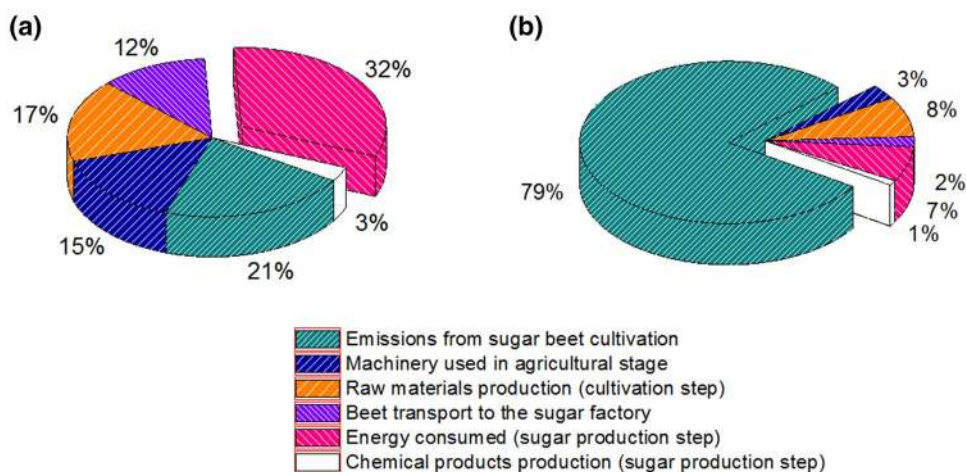**Fig. 3** Hydrolytic stability monitoring by **a** hardness and **b** contact angle tests

Fig. 4 **a** Total impact of the GHG emissions and **b** total NREU for PE_100% Bio-based compared to PE_75% Bio-based and PE_Fossil-based

Fig. 5 The total **a** phosphate and **b** nitrate contributions of all the steps of the sugar production

allocation where the 53% of the total impact corresponds to sugar beet cultivation and the 47% of the total impact corresponds to sugar production (see Supporting Information). As to the details of this analysis shown in Fig. 5a, those emissions to water mainly come from the energy consumed in the sugar production representing a 32% of the total impact followed by leaching formation from the beet cultivation (21% of the total). In the case of the energy consumed during the production, this phase represents the biggest impact due to the wastes caused from coal production. However, it should be noted that those emissions do not have a big impact on water due to clay soil, the dominating soil type in the southwest of Sweden, which reduces the phosphorus leakage. Nitrogen in nitrate form was also assessed. The total NO_3^- emission equivalent to economic allocation presented

a value of 3.2 kg NO_3^-eq/ton sugar and almost the same value for energy allocation (3.0 kg NO_3^-eq/ton sugar) as shown in Supporting Information. Figure 5b shows that 79% of these total emissions derive from the emissions to water as a consequence of leaching formation. The reason is the big amount of nitrogen used in fertilizers. The rest of the steps show a lower percentage of 9% being less representative. The total NREU and the total impact of GHG emissions in sugar production for all allocations were also studied and are shown in Supporting Information.

Conclusions

A new class of 100% bio-based polyester binder based on FDCA as precursors for PU coatings was re-designed and obtained through the selection and copolymerization of four different bio-monomers and cross-linked with a conventional IPDI based hardener. The technological evaluation showed a stiffer PU1 coating and a more hydrophilic character leading to better adhesion but also to a more moisture-sensitive surface. Potential applications may be interesting in the field of metal coating (coil coating, automotive), especially as intermediate layers/primers where the high adhesion of the material and recoatability are needed. The evaluation of the environmental impacts related to the production of the 100% bio-based polyester binder based on FDCA was applied in terms of GHG emissions and NREU. The substitution of Pht monomer with FDCA monomer in PE_100% compared to partial bio-based polyester (PE_75%) may reduce the total GHG emissions and NREU by around 36% and 38% respectively. In addition, a very remarkable reduction was showed for PE_100% compared to fossil-based polyester with a percentage of 79% in terms of GHG emissions and 60% in terms of NREU. However, other environmental burdens should be also studied to go deeper into this work.

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