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Upcycling of Agricultural Waste Stream to High-Molecular-Weight Bio-based Poly(ethylene 2,5-furanoate)

Jukka Niskanen,[a] Riitta Mahlberg,[a] Nicolaas van Strien,[a] Sari Rautiainen,[a] Essi Kivilahti,[a] Kari Koivuranta,[a] and Adina Anghelescu-Hakala*[a]

Orange peel and sugar beet pulp contain large quantities of pectin, which can be turned via galactaric acid into furan dicarboxylic acid (FDCA) and its esters. In this work, we show the polymerisation of these FDCA esters into high-molecular-weight, 70–100 kg/mol, poly(ethylene 2,5-furanoate) (PEF). PEF is an emerging bio-based alternative for poly(ethylene terephthalate) (PET), widely used in for example packaging applications. Closing the loop, we also demonstrated and confirmed that PEF can be hydrolysed by enzymes, which are known to hydrolyse PET, back into FDCA for convenient recycling and recovery of monomers.

Introduction

There is a significant push and need to replace fossil-based polymers and plastics with bio-based and renewable alternatives. 2,5-furandicarboxylic acid (FDCA) is a bio-based alternative to terephthalic acid, the latter is used in the production of poly(ethylene terephthalate) (PET).[1–3] PET and poly(butylene terephthalate) (PBT) are important and abundant polymers in our everyday commodities and lives. Polymers made from FDCA, e.g. poly(ethylene 2,5-furanoate) (PEF), share many of the properties such as high melting point, thermal stability, and crystallinity of PET and PBT. However, PEF has been reported to have superior gas barrier properties to PET, due to high crystallinity and limited chain mobility.[4–8] PEF and its analogues have also been shown to be enzymatically degradable under similar conditions to PET.[9–11] In addition to PEF, FDCA has been used in the preparation of a variety of polyesters and polyamides.[12–16]

High molecular weight polyesters (and polyamides) are produced in a two-step process. First a prepolymer is made as a melt. The molecular weight of the prepolymer is further increased in a solid-state polycondensation (SSP) step. In SSP, the ground prepolymer is heated above it glass transition temperature (T_g), while keeping the temperature below the melting temperature (T_m) of the polymer. SSP of PEF can be conducted at 180–205 °C, which is 15–40 °C below the melting point of the polymer.[17] For comparison, SSP of PET is conducted at 200–220 °C, which is 60–80 °C below the melting point.[18] The polycondensation occurs in the amorphous regions of the polymers and by-products (e.g. water or ethylene glycol) are removed by an inert gas flow or reduced pressure. Although the polycondensation in solid-state is significantly slower than in a melt polycondensation, SSP has several advantages: (1) Less side reactions are observed during extended reaction times as the reaction proceeds at lower temperature. (2) Interchain and transesterification reactions are limited. (3) An increase in the crystallinity and crystal perfection of the material is observed as the crystals dry during the process. In addition, in a melt polycondensation a sudden increase in viscosity can be observed as the molecular weight increases during the reaction, which could cause problems with the equipment used.[17–20]

Conventional method for preparation of FDCA is through oxidation of 5-hydroxymethylfurfural (HMF) which can be produced by dehydration of carbohydrates like glucose or fructose.[21] The disadvantages of this route are the instability of the intermediate HMF as well as the current use of edible sugar sources. Furthermore, FDCA is poorly soluble in industrial solvents, which hinders its purification and use.[22] Recently, we reported an alternative route to furancarboxylates using pectin-derived aldaric acids as intermediate.[1] This method uses pectin-containing waste streams, such as citrus peel and sugar beet pulp, to produce galactaric acid with over 95% yields based on pectin content.[23,24] The galactaric acid is further converted into furancarboxylates by acid-catalysed dehydration with over 80% yields.[1] An important step in the process is esterification of the intermediate galactaric acid by alcohol (e.g. MeOH or n-BuOH), which gives the corresponding FDCA esters as products.[1,25–29] Recently, furan-2,5-dimethylcarboxylate (FDMC) has received attention as an alternative monomer to produce PEF; the high solubility and low boiling point enable easier purification and processing compared to FDCA.[22,29] Furthermore, FDMC has been shown to result in PEF with less coloration due to decreased side reactions compared to FDCA.[30]

In this paper we report the polycondensation of ethylene glycol with FDCA butyl and methyl esters, prepared from bio-

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based galactaric acid. High-molecular-weight polymers (up to 113 kg/mol) are obtained by solid- or melt-state polycondensation of PEF prepolymers. In addition, we report on enzymatic degradation of PEF using enzymes that are known to digest PET.

Results and Discussion

Synthesis of Furandicarboxylate monomers

Monobutyl, dibutyl, and dimethyl furan-2,5-dicarboxylate (FMBC, FDBC, and FDMC, >97%) were prepared as reported by van Strien et al.[1,28,29] In a typical procedure for synthesizing FDMC, methanol, aldaric acid, and acid catalyst were weighed in a 10 L reactor. The reactor was sealed and pressurised to 5 bar with nitrogen. The reactor was heated to 235–240 °C for 4 h. The reaction was terminated by cooling down the reactor to room temperature, and the reaction mixture was filtered and washed with methanol. The solvents were evaporated from the liquid phase and the solids were dried in vacuo. The crude product was purified in a high-vacuum rotation distillation apparatus using total heated environment oven under reduced pressure (0-3 mbar). Fractions were collected between 60–150 °C. Further purification of some of the fractions was conducted by dissolving the product in acetone and precipitation in water. The obtained 2,5-FDMC (>97%) was analysed by ^{1}H-NMR and GC-FID. A detailed description of the synthesis of furandicarboxylates is presented as supporting information.

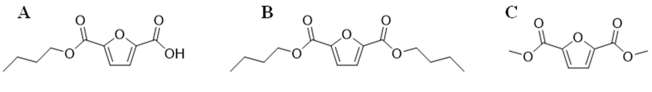
Low-Molecular-Weight Prepolymers

Prepolymers ($M_w = 10–47.9$ kg/mol, table 1) were prepared in melts using titanium(IV) isopropoxide as catalyst. Titanium(IV) isopropoxide was chosen as the catalyst as it has been shown to have a higher reaction rate than e.g. tetrabutyltitanate or dibutyltinoxide.[17] The polymerizations were conducted under reduced pressure, where the pressure was reduced from atmospheric to 0.2 kPa during the polymerization procedure.[8,17] The monomers for these polymers were obtained from aldaric acid produced by in house fermentation from pectin (yielding in fully biobased monomer), commercial aldaric acid, or for comparison from Biosynth Carbosynth.[24,28] The molecular weight of the prepolymers was later increased ($M_w = 40–113$ kg/mol, table 2) in a polycondensation step in solid- or melt-state. Prepolymers were prepared from monobutyl-, dibutyl, and dimethyl esters of FDCA (FMBC, FDBC, and FDMC, respectively, Scheme 1). The polycondensation includes several stages: In the initial stage of the polycondensation mainly butanol and methanol are distilled off from the reaction mixture, as the FDCA esters undergo transesterification with ethylene glycol (EG) under atmospheric pressure at 175 °C. In a later stage, when the temperature is increased to 200 °C and the pressure reduced to 0.6–0.2 kPa, EG is distilled off; first the excess of EG followed by EG released during the polycondensation.[8] No significant differences in reactivity were observed between FMBC, FDBC, and FDMC during the polycondensations. However, FMBC was observed to have some surfactant properties causing the solution of FMBC in EG to foam when applying vacuum to the solution. Zhu et al. conducted this first step of the polycondensation of poly(butylene terephthalate) under N_2 atmosphere and longer reaction times for the three stages of the reaction.[8] Their first stage was performed at 150 °C for 2 hours, the second at 175 °C for 12 hours, and the third step at 200 °C for 8 hours.[8] By reducing the pressure during the second and third stage of the polycondensation we could reduce the reaction time from 18 hours to 5 hours. It should be noted that poly(butylene terephthalate) has a lower melting point (173 °C) than PEF (203-219 °C), hence the latter stages of the polycondensation occurred in a melt, whereas the last stage in the polycondensation of PEF the polymer solidified. Regardless, the molecular weight of the obtained polymers we obtained were

Table 1. Summary of prepolymers produced from monobutyl, dibutyl, and dimethyl esters of FDCA (FMBC, FDBC, and FDMC). Reaction time was 5 h for each polymerization.

ID	FDCA-ester/EG/Catalyst[a]	M_w (g/mol)[b]	Đ[b]	DEG (%)[c]	m (g) [d]
Monobutyl ester of FDCA (FMBC)					
PrePEF-MB1	1/2/0.015	15900	2.5	3	8.6
PrePEF-MB2	1/3/0.015	17100	3.1	5	8.4
PrePEF-MB3	1/4/0.015	18900	3.0	4	8.1
PrePEF-MB4	1/3/0.015	14800	2.9	6	17.5
Dibutyl ester of FDCA (FDBC)					
PrePEF-DB1	1/3/0.019	24500	3.5	13	2.6
PrePEF-DB2	1/3/0.019	17400	2.8	8	17.1
PrePEF-DB3	1/3/0.019	14500	2.4	11	29.0
PrePEF-DB4	1/3/0.019	13700	2.4	7	27.6
PrePEF-DB5	1/3/0.0095	47900	4.1	20	1.6
Dimethyl ester of FDCA (FDMC)					
PrePEF-DM1	1/1.5/0.013	10500	3.1	4	49.9
PrePEF-DM2	1/1.2/0.013	10400	3.1	1	46.0
PrePEF-DM3	1/2/0.013	10000	3.3	3	48.2
PrePEF-DM4	1/2/0.013	11400	3.3	22	52.8
PrePEF-DM5	1/2/0.013	20300	2.0	4	47.2
PrePEF-DM6	1/2/0.013	19400	1.8	2	41.8
PrePEF-DM7	1/2/0.013	17400	1.8	3	45.5
PrePEF-DM8	1/2/0.013	14500	3.3	3	15.6
PrePEF-DM9	1/1.2/0.013	12000	2.9	2	48.2
PrePEF-DM11	1/2/0.0095	26200	2.0	0	9.8

[a] monomer/catalyst ratio, [b] molecular weight and dispersity, [c] diethylene glycol content (DEG), and [d] mass of obtained polymers.



Scheme 1. The chemical structures of (A) monobutyl-, (B) dibutyl, and (C) dimethyl-FDCA esters (FMBC, FDBC, and FDMC, respectively)

Table 2. Summary of the high-molecular-weight polymers.

ID	M_w (g/mol)[a]	Đ[a]	Time (h)[b]	T_g (°C)[c]	T_m (°C)[d]	DEG (%)[e]	m (g)[f]
Solid-State Polycondensations							
PEF-1[g]	65 700	2.7	24	87	213	5	44.7
PEF-2[g]	42 200	1.9	24	85	217	1	43.7
PEF-3[g]	56 500	2.3	24	87	213	4	41.9
PEF-5[g]	39 600	2.1	24	86	207	4	43.7
PEF-6[g]	44 600	2.2	24	88	211	5	37.3
PEF-7[h]	58 400	2.8	24	87	210	4	41.6
PEF-8[h]	45 900	2.4	24	82	219	4	15.1
Melt-State Polycondensations							
PEF-4M[g]	91 000	4.1	24	80	211	22	35.4
PEF-7M[g]	93 600	3.9	24	89	195	6	19.8
PEF-9M[g]	98 300	4.0	24	87	205	5	2.7
PEF-10M[i]	73 800	3.9	11.5	86	200	11	9.3
Batch-1M (PEF-1 + PEF-5) [g]	113 000	7.4	24	88	203	6	49.3
Batch-2M (PEF-3 + PEF-6[g]	108 700	12.4	24	88	216	6	40.9

[a] Molecular weight and dispersity, [b] reaction time, [c] glass transition temperature, [d] melting temperature, [e] diethylene glycol content (DEG), and [f] mass of obtained polymers. The monomers for these polymers were obtained either from commercial [g] aldaric acid, [h] aldaric acid produced by fermentation in house from pectin, or [i] commercial sources.

in the range of what was obtained by Zhu et al. (16-65 kg/mol).[8] Also the reported colour of the polymers, light yellow to brown, was the similar to the colour of our polymers.

The polycondensations were conducted with an excess of EG to FDCA. The monomer ratios were varied between 1:1.2 to 1:4 FDCA/EG, for comparison Zhu et al. used a ratio of 1:3.[8] Diesters of FDCA are more soluble in EG, than FDCA or the monoester, thus lower amounts of EG could be used in the polycondensations. For comparison, up to 1:3 ratio of FDCA:EG are needed due to the poor solubility of FDCA.[31,32] Prepolymers with similar molecular weights and dispersities were obtained, regardless of the FDCA/EG ratio (table 1).

The formation of diethylene glycol (DEG) during polycondensation of PET or PEF is a known side reaction.[31–37] The DEG content can be determined from ^{1}H-NMR spectra (figures 1 and 2). The DEG contents for all pre-polymers and polymers were calculated using the signals at 3.85, 3.94, and 3.98 ppm and are presented in tables 1 and 2, as described by Banella et al.[31] In the ^{1}H-NMR spectra, the signals 3.94 and 4.48 ppm are assigned to DEG, the signal at 3.86 ppm to the methyl end groups, and the signals at 3.98 and 4.43 ppm to ethylene end groups.[36,38] The number of methyl end groups was higher in polymers obtained with a lower monomer FDCA/EG (1.2–1.5) ratios. It should be noted that the signals at 4.43 and 4.48 ppm overlap with the ^{13}C satellite signal from the ethylene groups in the polymer, thus they should not be used in the determination of DEG or end group content, and the DEG or end group content, but the signals at 3.86, 3.94, and 3.98 ppm instead. The assignation was confirmed by letting the end groups react with trifluoro acetic acid, as described by Kenwright et al, and the signals from the ethylene end groups disappear during the reaction (3–6 days) leaving behind the ^{13}C satellite and the DEG

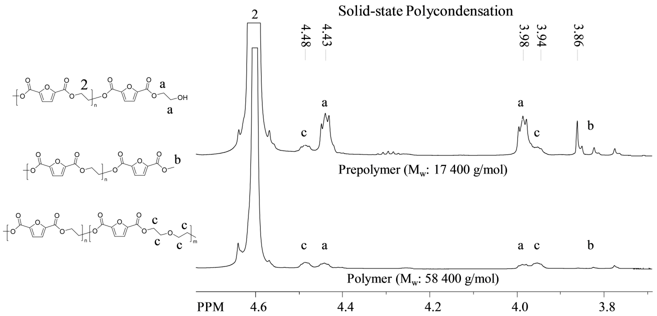


Figure 1. Close up of the aliphatic region of ^{1}H-NMR spectra of PrePEF-DM7 (M_w: 17 400 g/mol) and final polymer (PEF7, M_w: 58 400 g/mol) after solid-state polycondensation, showing the ethylene glycol end groups (a), methyl (b) end groups, and diethylene glycol repeat units (c) of the polymers. As the molecular weight of the polymers grows, the number of end groups diminish.

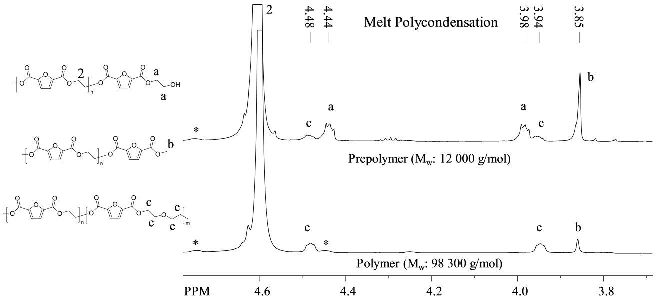


Figure 2. Close up of the aliphatic region of ^{1}H-NMR spectra of PrePEF-DM9 prepolymer and final polymer (PEF9 M) after melt polycondensation, showing the ethylene glycol end groups (a), methyl (b) end groups, and diethylene glycol repeat units (c) of the polymers. As the molecular weight of the polymers grow, the number of end groups diminish. The ^{13}C satellites from the signal 4.6 ppm are indicated with asterisks (*).

signals (Supporting Information, figure S4).[36] PEF is poorly soluble in common solvents, hence a 1:1 mixture of TFA-d and $CDCl_3$ was used for NMR samples. It should be noted that all samples were analysed within 20 min of preparing the samples, to minimize the contribution of the esterification reaction between TFA-d and the ethylene end groups.

The prepolymers contained 1 to 5% DEG (table 1) and the final polymers obtained by SSP 1 to 6% (table 2). A considerably higher DEG content was observed with PrePEF-DB5, PrePEF-DM4, and PEF-4 (20 to 22%). The divergence of this polymer from the others may be attributed to the purity of the FDMC used in the synthesis. The FDMC used in the polycondensation of PrePEF-DM4, contained 5.9% monomethyl FDCA, 6.7% furan-2,3-dicarboxylate esters, and 86.4% FDMC (Supporting Information figure S5 and S6). The FDMC used in the other polycondensations contained $<1\%$ of furan-2,3-dicarboxylate esters, $<2\%$ of monomethyl FDCA ester, and $>97\%$ FDMC. Commercially available FDMC ($>98\%$) was used as a control in the polycondensation of PEF-2, which also had the lowest DEG content (1%). The esterification and transesterification rates of the monomethyl FDCA (esterification and transesterification) and dimethyl FDCA (FDMC, transesterification) with EG are different. In addition, the direct esterification of FDCA is often conducted at higher temperatures (200–250 °C) than the transesterifications of FDMC (160–190 °C).[32] We speculate that since the direct esterification is slower at the temperature used in the transesterification step (175 °C), the coupling of EG is slightly favoured, resulting an increased DEG content.

Even small amounts (1–2%) of DEG are known to affect the crystallinity, melting point, glass transition temperature, light stability, susceptibility towards aqueous hydrolysis and thermal degradation, and the dying of PET.[33,34,37] For example, the melting point is lowered by 5 °C with each weight percent of DEG in the PET.[33,37] Unfortunately, the etherification of hydroxyethyl end groups is catalysed by the same catalyst that catalyse the polycondensation of PET and PEF. The amount of DEG can be reduced by the lowering the amount and type of catalyst and reaction temperature.[31–35] Our results also indicate that the presence of 2,3-FDCA esters increases the DEG content in the final polymers. A slight increase in the DEG content was also observed with increasing amount of EG or catalyst (table 1). Detailed studies regarding the presence of 2,3-FDCA esters and monoester on the polycondensation and on the polymer properties of PEF will be part of future research.

High-Molecular-Weight Polymers

The molecular weight of the pre-polymers was increased in a polycondensation step either at 195 °C or at 225 °C. The reaction can be monitored by ^{1}H-NMR spectra, as the number of end groups diminish during the polycondensation. In solid-state polycondensation (SSP) at 195 °C, the polycondensation can only occur in the amorphous regions of the polymer. Although the polycondensation is limited to the amorphous regions of the polymer, increasing the temperature influences the molecular weights achieved. Kasmi et al. have shown that increasing the temperature from 190 to 205 °C also increased the M_n from 8000 to 13 000 g/mol.[17] The temperature for SSP (195 °C) was chosen so that it was close to T_m, but would not melt the polymer or result in the granules excessively adhering to each other. While at 225 °C, in the melt-state polycondensation (MSP), and the polycondensation is not limited by the crystalline parts of the polymer. The M_w of the polymers increased from 10–20 kg/mol to 42–66 kg/mol during the SSP, accompanied by a slight increase in the DEG content (1–2%-units). The increase in molecular weight was higher in the melt polycondensations, yielding in 91–98 kg/mol polymers (figure 3). However, the MSP resulted in a higher increase (2-3%-units) in the DEG content. We believe this increase in the DEG content is due to coupling of –OH end groups. The increase in the DEG is affected by the higher temperature and therefore the higher mobility of the end groups in the melt during MSP.

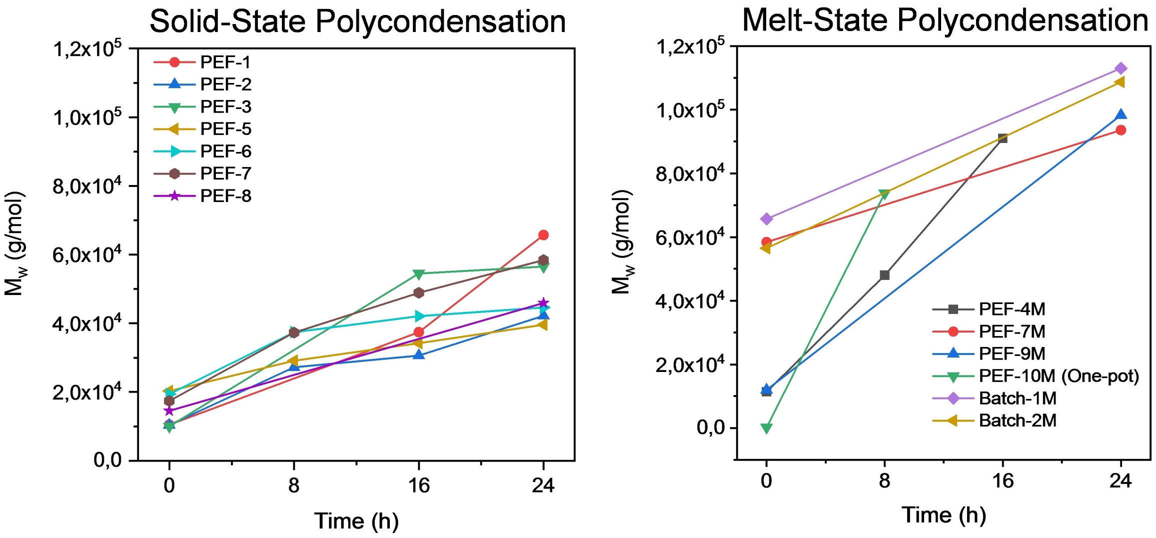


Figure 3. Evolution of molecular weights of PEF samples during solid- and melt-state polycondensation of prepolymers.

Due to the high amount of DEG in PrePEF-DM4 (22 %), the melting temperature of the polymer was significantly lower (172 °C) than for the other prepolymers (208-215 °C). Hence the prepolymer melted at 195 °C and underwent melt-state polycondensation. After 16 hours at 195 °C, the M_w of PEF-4 M was 91 kg/mol, significantly higher than what was observed for PEF1-8 after SSP (M_w 40–66 kg/mol, table 2). The M_w of PrePEF-DM9 was increased from 12 kg/mol to 98 kg/mol during 24 hours at 225 °C, while only a slight increase of the dispersity from 2.9 to 4.0 was observed. The reaction was continued for 24 more hours. However, after 48 hours at 225 °C, the polymer turned insoluble in HFIP or TFA due to extensive crosslinking. In addition, the polymer had turned black. Color changes of PEF has been observed before, especially when exposed to high temperatures for extended periods of time. These color changes are due to decarboxylation of the FDCA but can also originate from sugar residues in the monomers.[31,39,40] In our case, as the monomers were purified extensively and no sugar residues could be observed by GC-FID, we attribute the color change to decarboxylation and oxidation.

PEF-10 M was prepared in a one-pot reaction, where the prepolymer was not isolated but subjected instead to polycondensation in a melt at 225 °C for 8 hours, similar to the process described by Zhu et al.[8] A 74 kg/mol polymer was obtained with similar dispersity (3.9) to PEF-4 M and PEF-9 M. The reaction was in essence a duplicate of PEF-2, hence we were surprised with the high DEG content of the polymer (11 %). We speculate that this is due to catalyst and oligomers, which were not removed from the polymer. During the isolation of the other prepolymers they were purified by precipitation, a step that would remove both oligomers from the samples, but also any free dimerized ethylene glycols and some of the catalyst that may have been present in the sample.

The increase in the dispersity of the polymers during the polycondensation in a melt state is due to interchain reactions, where an end group of a polymer reacts with a repeating unit of another polymer. These interchain reactions often yield in one shorter and one longer polymer and the dispersity of the polymer increases.[20]

The M_w of selected PEF samples was further increased by subjecting the polymers to a second polycondensation step as melts, after SSP. The M_w of PEF-7 was increased from 58 kg/mol to 94 kg/mol during 24 h at 225 °C, accompanied by a slight increase in dispersity from 2.8 to 4.0.

Two batches were made by combining PEF-1 with PEF-5 (Batch-1 M) and PEF-3 with PEF-6 (Batch-2 M) in melt-state polycondensations, yielding in 113 kg/mol (Batch-1 M) and 108 kg/mol (Batch-2 M) polymers. However, both polycondensation resulted in a significant increase in the dispersity of the polymers from 2.1–2.7 to 7.4–12.4.

Thermal Characterisation

PEF is a highly crystalline and rigid polymer, with reported glass transition (T_g) at 75–80 °C, crystallisation (T_c) at 165 °C, and melting temperatures (T_m) at 210–215 °C.[4,41,42] Similarly, our polymers exhibited T_g at 73–87 °C, T_c at 125–167 °C, and T_m at 208–219 °C (figure 4A). However, the T_c was not detected for all samples (Supporting Information, figures S8-S9). Many of the polymers were also observed to have several melting temperatures (204-226 °C), but also low temperature melting at 116–147 °C. After heating the samples above the melting temperature (250 °C), the low temperature melting endothermic peaks disappear (Supporting Information, figure S9). The multiple melting endotherms at 204 to 226 °C also fuse into one melting endotherm, as is observed with PrePEF-DM8 (figure 4B). Similarly, to what has been reported by Righetti et al and Papageorgiou et al.[43,44] In most of the high molecular weight samples, no melting endotherm is observed after annealing at 250 °C, likely due to insufficient time for the polymers to organize into crystals during the experiment. As the M_w increases during SSP or MSP polycondensation, the T_g is shifted to slightly higher temperatures from 73–82 °C to 82–87 °C (supporting information, table S5).

The crystallisation of PEF is much slower than that of PET, due to the greater stiffness of the furan ring, hence the T_c and T_m could only be observed during the first heating cycle for

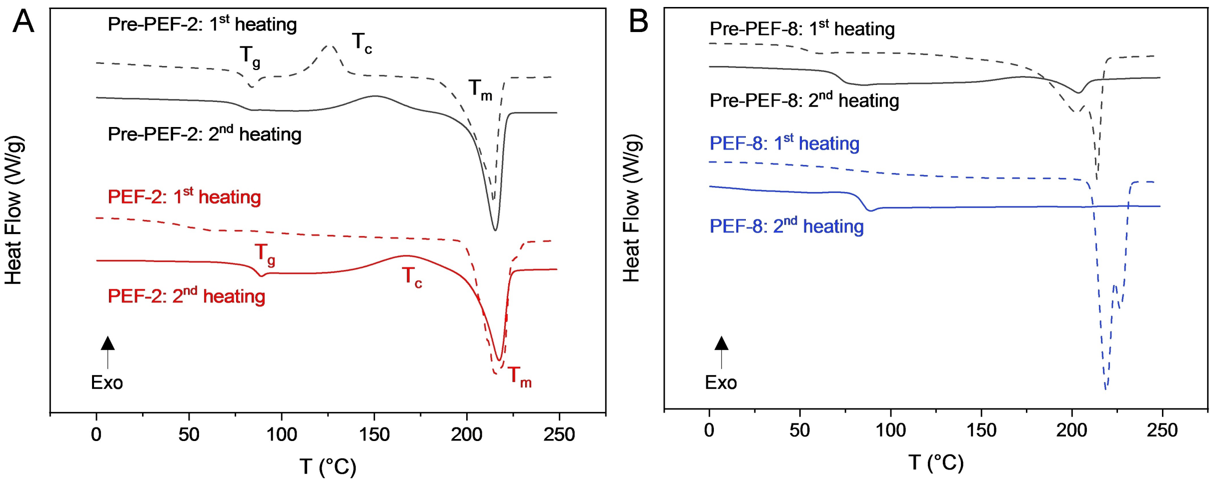


Figure 4. DSC thermogram of PrePEF-DM2, PrePEF-DM8, PEF-2, and PEF-8.

many of our samples.[4,42] Furan based polymer have also been reported to have several melting temperatures, a common feature of semi-crystalline polymers.[43–46] Poly(propylene 2,5-furanoate) has been reported to have up to four melting temperatures.[43,45] These melting temperatures result from the presence of several types of crystals in the polymers.[43–45] There may also be orientation effects and segregation of the polymers with different molar masses during crystallisation and annealing, but also melting, fusion, and recrystallisation during melting and annealing.[43–45] In addition, there may be crystals in the polymers originating from metastable crystals, as has been reported for PET, and are observed as a endothermic peak at a temperature lower than the melting temperature of the polymer.[47]

Mechanical Properties

The mechanical properties of injection moulded samples of PEF-7 M and PEF-9 M show that the obtained materials are hard and brittle materials with Young's moduli of 3.8 and 3.6 GPa, tensile strength of 40.7 and 29.8 MPa, and 1.2 and 0.6% elongation at break, respectively (table 3). The tensile strength for both PEF-7 M and PEF-9 M were lower than what was measured for PET (55.2 MPa). Whereas the Young's modulus was higher for both PEF samples than what was observed for PET (2.4 GPa). The strain at break was lower for the PEF samples than for PET (3.6%). Xi et al. and Jiang et al report similar observation for PEF.[48,49] Although the molecular weights of PEF-7 M and PEF-9 M are similar they have slightly different DEG contents (and different melting temperatures (table 2). The DEG content is known to significantly affect the crystallinity and mechanical properties of PEF.[33,34,37] The 1% higher DEG content in PEF-7 M resulted in both higher tensile strength and strain at break, in comparison to PEF-9 M.

Table 3. Mechanical properties of selected PEF samples and PET.

Sample	Young's Modulus (Gpa)	Tensile strength (Mpa)	Strain at break (%)
PEF-7M	3.8	40.7	1.2
PEF-9M	3.6	29.8	0.6
PET	2.4	55.2	3.6

Enzymatic Degradation of PEF

Enzymatic degradation of PEF was conducted using AdPETase and IsPETase enzymes, which have been shown to degrade PET.[50,51] The enzymatic degradation was conducted for 7, 24, or 48 hours, with 25 μg/mL of the enzymes present. The signal attributed to FDCA in the RP-HPLC trace was identified using a reference molecule. Other degradation products observed in the RP-HPLC trace was identified as PEF degradation products with UPLC-MS, based on the characteristic ions of FDCA with m/z 139; 157.01; and 183.03. Degradation products presenting FDCA and oligomers can be observed in RP-HPLC traces (figure 5A) indicating that PEF is hydrolysed enzymatically into a variety of products, including mono(2-hydroxyethyl) furanoate, and bis(2-hydroxyethyl) furanoate.[9] However, the exact structure of the PEF oligomers could not be determined. The amount of released FDCA also increases with the hydrolysis time (figure 5B). The total peak areas, peaks 1 to 7 from RP-HPLC chromatograms, of PEF samples degraded by AdPETase and IsPETase for 7, 24, and 48 hours are presented as supporting information (figure S10). No significant difference in total peak areas was observed between IsPETase and AdPETase, indicating that the total amount of degradation products released by the enzymes was similar. Aqueous hydrolysis of PEF was ruled out, as no changes in the controls incubated without enzymes were observed.

The molecular weight of the PEF was determined after the enzymatic hydrolysis. An increase in M_n of the PEF was observed

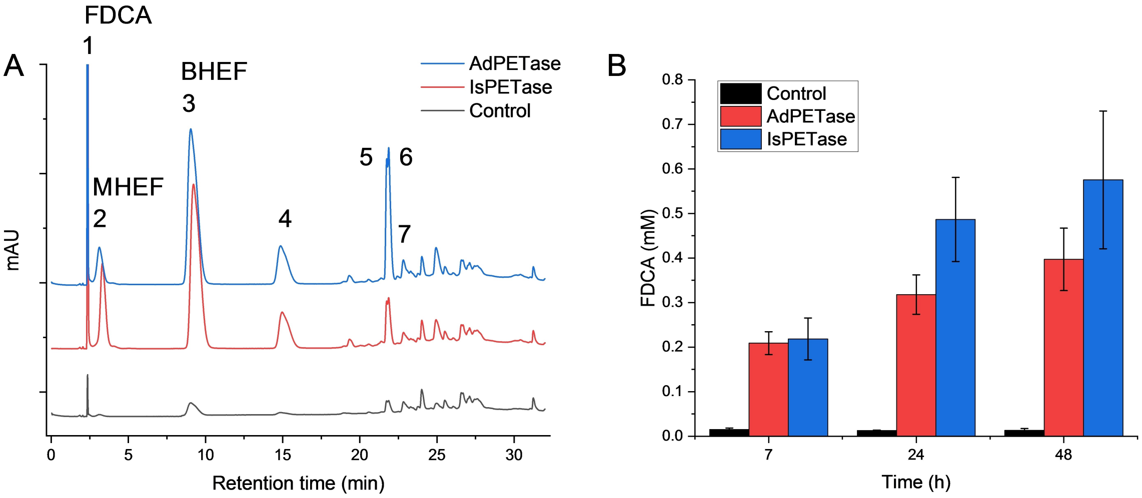


Figure 5. A. RP-HPLC chromatogram after 48 hours of hydrolysis. The number-labelled peaks are the degradation products used to confirm degradation: 1 is furan dicarboxylic acid (FDCA), 2 and 3 are mono(2-hydroxyethyl) furanoate (MHEF) and bis(2-hydroxyethyl) furanoate (BHEF), and 4–7 are PEF oligomers. B. Production of FDCA during degradation of PEF by AdPETase and IsPETase.

from 8 300 (control) to 11 000 g/mol (IsPETase and AdPETase hydrolysed samples), while M_w decreased from 47.9 to 40.5 kg/mol, and the dispersity of the polymer decreased from 4.1 to 3.8. The increase in M_n indicates that small molecular fractions of the polymer were hydrolysed into oligomers and other water-soluble species, which shifts the distribution towards higher molecular weights (Supporting Information, figure S11).

For polymers that are insoluble in water, such as PEF, the degradation process occurs on the surface of the polymer particles in the aqueous dispersion. The process starts by adsorption of the enzyme on the particles surface.[52,53] Once the enzyme has adsorbed on to the surface, the hydrolysis can start. As the hydrolysis proceeds, more and more of the surface is eroded as the polymer is turned into oligomers and other low-molecular weight species becoming eventually water soluble.[54] The rate of hydrolysis, and subsequent erosion, is different for crystalline and amorphous regions in the polymer due to the accessibility of the hydrolysable groups in the polymer to the enzyme.[55]

Conclusions

In this paper, we demonstrated that butyl or methyl esters of FDCA, prepared from galactaric acid, can be turned into high molecular weight PEF. The FDCA esters were produced by solid acid catalysed dehydration using galactaric acid as stable intermediate. Galactaric acid can be produced from pectin via a oxidative fermentation, enabling the use of pectin-containing agricultural side streams, such as citrus processing waste or sugar beet pulp, in production of biobased polymers.

The monobutyl, dibutyl, and dimethyl esters of FDCA were used in preparing prepolymers. No significant differences in the reactivity of the FDCA esters were observed in the polycondensations. The prepolymers were successfully turned into high molecular weight polymers in a polycondensation step conducted either in a solid- or melt-state process. The M_w was increased from 20 kg/mol to 90–100 kg/mol in melt-state polycondensation, whereas 70 kg/mol polymers were obtained in solid-state polycondensation.

Closing the circle, we also demonstrated and confirmed that PEF can be hydrolysed by enzymes, which are known to hydrolyse PET, back into FDCA.

Supporting Information

The authors have cited additional references within the Supporting Information.[56,57]

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Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords: poly(ethylene 2,5-furanoate) · bio-based · polycondensation · enzymatic degradation · furan dicarboxylic acid

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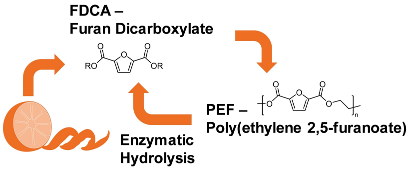
RESEARCH ARTICLE

Orange peel and sugar beet pulp contain pectin, which can be turned into furan dicarboxylic acid (FDCA) and its esters. In this work, we show the polymerisation of these esters into high-molecular-weight poly(ethylene 2,5-furanoate) (PEF). PEF is an emerging bio-based alternative for poly(ethylene terephthalate) (PET). Closing the loop, we also demonstrated and confirmed that PEF can be hydrolysed by enzymes.



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1 – 9

Upcycling of Agricultural Waste Stream to High-Molecular-Weight Bio-based Poly(ethylene 2,5-furanoate)