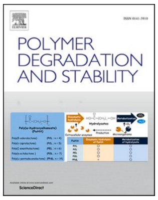
Title	Synthesis of bio-based poly(diethylene furanoate)-block-polylactide copolymers with UV blocking properties
Author(s)	Molnár, Judit Rebeka; Hsu, Yu I.; Uyama, Hiroshi
Citation	Polymer Degradation and Stability. 2025, 238, p. 111342
Version Type	VoR
URL	https://hdl.handle.net/11094/101391
rights	This article is licensed under a Creative Commons Attribution 4.0 International License.
Note	

Polymer Degradation and Stability 238 (2025) 111342

Contents lists available at ScienceDirect

Polymer Degradation and Stability

journal homepage: www.journals.elsevier.com/polymer-degradation-and-stability



Synthesis of bio-based poly(diethylene furanoate)-block-polylactide copolymers with UV blocking properties

Judit Rebeka Molnár, Yu-I Hsu *, Hiroshi Uyama *

Department of Applied Chemistry, Graduate School of Engineering, Osaka University, 2-1 Yamadaoka, Suita, Osaka, 565-0871, Japan

A R T I C L E I N F O

Keywords:
Biopolymer
Polylactic acid
Poly(diethylene 2,5-furanoate)
2,5-furandicarboxylic acid
multiblock copolymer
UV blocking
Ring-opening polymerization

A B S T R A C T

The transition to a circular economy requires the development of bio-based polymers with enhanced functionality to compete with conventional oil-sourced materials. In this study, a bio-based furandicarboxylic acid-containing polyester, poly(diethylene furanoate) (PDEF) was directly copolymerized with polylactide (PLA) for the first time, through the polycondensation of dimethyl furan-2,5-dicarboxylate (MFDC) and diethylene glycol (DEG), used as an initiator for the ring-opening polymerization (ROP) of lactide, followed by chain extension reaction with hexamethylene diisocyanate (HDI) to obtain poly(diethylene furanoate)-block-polylactide (PDEF-b-PLA) alternating multiblock copolymers. The PDEF synthesized with different reaction times exhibited an average glass transition temperature (T_g) of 33.8 °C. The copolymers had PLA segment lengths of 1000 and 300 g/mol after ROP maintaining an amorphous structure with a T_g of 34.5 and 33.3 °C respectively, suggesting easy processability. Thermal stability of the copolymers was enhanced, indicated by increased decomposition temperatures and residual weight compared to neat PLA. PDEF displayed elastomer-like behavior while the copolymerization resulted in an intermediate behavior between PDEF and semi-crystalline PLA, with a high Young's modulus of 1.7 and 1.4 GPa, a balanced tensile stress at yield of 24.3 and 28.9 MPa and a significantly increased elongation at break, by 700–1100 % compared to neat PLA. All PDEF-containing samples demonstrated excellent UV-blocking ability due to the furan moiety, effectively blocking UV radiation below 300 nm while maintaining transparency in the visible range. These bio-based PDEF-b-PLA copolymers offer a sustainable alternative for applications such as food packaging and coatings, where thermal stability, mechanical resilience and UV protection are essential.

1. Introduction

To combat climate change and preserve our resources for future generations, the world is transitioning to a circular economy, which is a critical tool to achieve the United Nations' Sustainable Development Goals by 2030. However, to fully embrace circularity, the production of polymers has to shift from oil-sourced to bio-based, but to achieve broader adoption, they must compete effectively with their petrochemical counterparts.

Among the potential bio-based building blocks, 2,5-furandicarboxylic acid (FDCA), an aromatic carboxylic acid derived from plant-based sugar [1,2] stands out and is already commercially produced by Avantium [1]. FDCA serves as a bio-based alternative to terephthalic acid, a key building block widely used in polyesters. When comparing polyethylene terephthalate, derived from terephthalic acid and ethylene glycol, with its FDCA based counterpart, polyethylene furanoate, the latter exhibits a higher Young's modulus, higher tensile strength, and superior gas barrier properties [3]. Furthermore, FDCA and its copolymers have been utilized in various applications, including elastomers [4,5], polyester polyols [6], polymers with flame retardant [7,8] and self-healing properties [9] and coatings [10]. FDCA remains expensive due to its limited commercial availability as of now. On the other hand, polylactic acid (PLA) is the most produced bioplastic with the biggest share in the packaging, textiles, and agriculture segments. However, its thermal and mechanical properties, as well as its optical properties, require improvement. Thus, copolymerizing PLA with an FDCA-derived polyester offers the potential to enhance these properties or introduce novel functionalities to the resulting copolymer.

There have been attempts to improve the properties of PLA with FDCA-derived polyesters. For instance, Xie et al. synthesized FDCA with 1,6-hexanediol to obtain poly(hexamethylene 2,5-furandicarboxylate. The resulting polymer exhibited Young's modulus of 0.67 GPa, tensile

---

* Corresponding authors at: Department of Applied Chemistry, Graduate School of Engineering, Osaka University, 2-1 Yamadaoka, Suita, Osaka, 565-0871, Japan.
E-mail addresses: yuihsu@chem.eng.osaka-u.ac.jp (Y.-I. Hsu), uyama@chem.eng.osaka-u.ac.jp (H. Uyama).

https://doi.org/10.1016/j.polymdegradstab.2025.111342
Received 15 February 2025; Received in revised form 22 March 2025; Accepted 25 March 2025

strength at break of 30 MPa, and 237 % elongation at break, demonstrating elastomer-like behavior that could improve the brittleness of PLA [11]. Similarly, blends of PLA with poly(pentamethylene 2,5-furanoate) (PPeF) [12], poly(butylene furan 2,5-dicarboxylate) (PBF), and poly(butylene adipate) [13] showed immiscibility, as evidenced by SEM micrographs displaying typical sea-island structure. The elastic modulus, tensile stress at yield, and stress at break decreased with increasing PPeF content, while strain at break increased, which could be optimized through copolymerization. While direct blending with tough polymers or compounding with low-molecular-weight plasticizers is a common method to address the intrinsic brittleness of PLA, it often results in reduced strength and modulus. Therefore, direct copolymerization offers a more effective approach, allowing properties to be finely tuned through molecular design.

The blocking of UV radiation is necessary for many UV-sensitive applications, such as food packaging, photovoltaic cells or coatings. The presence of conjugated double bond sequences in the furan and carbonyl groups promotes the UV-blocking ability of furan-based polymers [14]. For example, Sun et al. synthesized PPeF, which was chain extended by hexamethylene diisocyanate (HDI). The resulting PPeF-HDI showed a UV cut-off from 300 nm, which was further improved with the addition of 0–20 wt % lignin [15]. In PPeF-PLA blends, as little as 1 wt % PPeF significantly reduced transmittance in the UVC and UVB regions (225–325 nm) [12]. The incorporation of 2,2′-bifuran-5,5′-dicarboxylic acid into the polyester structures greatly enhanced their UV-absorbing properties, making the bifuran unit an interesting multifunctional monomer. Polyesters copolymerized with bifuran moieties and polyethylene terephthalate effectively blocked most of the UV-A spectrum (400–320 nm) and completely prevented the transmission of UV-B (320–275 nm) and UV-C (275–200 nm) spectra [16]. Furthermore, polyester synthesized from the bifuran unit and ethylene glycol demonstrated a similar UV-blocking ability, extending across the entire UV-A range [17].

This research aimed to directly copolymerize a poly(alkoxy furanoate) with PLA for the first time to improve the optical, thermal and mechanical properties of PLA by incorporating poly(diethylene furanoate) PDEF through the creation of alternating multiblock copolymers. Since the polycondensation of high molecular weight polyesters require long processing time, high temperature, and low vacuum conditions, preparing low molecular weight FDCA-based polyesters offer a less energy-intensive approach. One of the key sustainable aspects of this synthesis method is that it can be carried out in bulk using melt polymerization, without the need for solvents even in the chain extension reaction. In this study, PDEF was used to initiate the ROP of lactide to obtain PLA-PDEF-PLA triblock prepolymers, that were chain-extended by HDI to increase the molecular weight. In the obtained novel bio-based PDEF-b-PLA alternating multiblock copolymer, PDEF was expected to increase the thermal stability and the toughness compared to neat PLA and improve the UV shielding through the furanic moiety.

2. Materials and methods

2.1. Materials

2,5-furandicarboxylic acid (FDCA) was purchased from Apollo Scientific Ltd. PLA (Ingeo™ 2003D) (M_n =89,000 g/mol, PDI = 2.2 measured by GPC) was purchased from Nature Works LLC (Nebraska, USA). Dibutyltin oxide (DBTO), hexamethylene diisocyanate (HDI), L-lactide (LA), and phenyl isocyanate were purchased from Tokyo Chemical Industry Co. (Tokyo, Japan). Diethylene glycol (DEG), deuterated chloroform, chloroform for GPC, super dehydrated dimethyl sulfoxide (DMSO), super dehydrated methanol, tin(II)-ethyl hexanoate ($Sn(Oct)_2$), super dehydrated toluene, were purchased from Fujifilm Wako Pure Chemical Co. (Osaka, Japan). All reagents were used as received.

2.2. Synthesis of PDEF and derivatives

2.2.1. Synthesis of dimethyl furan-2,5-dicarboxylate (MFDC)

FDCA was converted into MFDC using the Fischer esterification method as described in Papageorgiou et al. [18]. Briefly, FDCA (50 g, 0.32 mol) and anhydrous methanol (641 mL, 15.81 mol) were transferred to a 500 mL eggplant flask. Concentrated H_2SO_4 (6.41 mL, 0.12 mol) was added dropwise to the mixture. The flask, equipped with a condenser and a magnetic stirring bar was heated to reflux at 80 °C for 6 h. After cooling, the residual methanol was evaporated under reduced pressure. The H_2SO_4 was neutralized with a 10 % w/v Na_2CO_3 solution, and the mixture was vacuum filtered. The resulting white powder was recrystallized overnight from a 50:50 v/v mixture of methanol and distilled water. The recrystallized product was vacuum filtered and washed with methanol. Finally, the needle-shaped crystals were dried in a vacuum oven at 50 °C.

2.2.2. Synthesis of PDEF

PDEF was synthesized using the following materials and ratios: MFDC (20 g, 0.109 mol, 1 eq.), DEG (20.581 ml, 0.217 mol, 2 eq.), and DBTO catalyst (0.011 g, 0.0043 mmol, 400 ppm). These reagents were placed in a three-neck round-bottom flask equipped with a mechanical stirrer, a distillation head, a collector flask, and an inlet to the Schlenk line. The mixture was dried for 3 h. For the transesterification phase, the temperature was raised to 160 °C and maintained for 4 h under a nitrogen atmosphere, until the distillation of methanol was complete.

During the subsequent polycondensation phase, the temperature was maintained at 160 °C while the pressure was sequentially reduced to 13,000 Pa and then to 2000 Pa for two hours in each step. In the last step, the pressure was further reduced to <20 Pa for various reaction times. After the completion of the reaction, the mixture was quenched, and the viscous solution was dissolved in chloroform and precipitated in cold methanol. The precipitate was filtered and vacuum-dried at room temperature.

2.2.3. Synthesis of PDEF end-capped with phenyl isocyanate

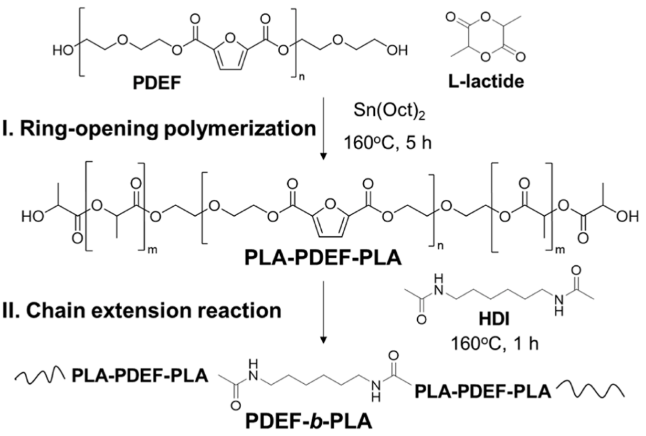
In a 25 ml dry two-neck flask 0.5 g PDEF was dried for 1 h in vacuum. During this period, a 0.1 g/ml toluene solution of $Sn(Oct)_2$, at 1 mol % relative to PDEF, was added. Around 3 ml of anhydrous DMSO was added under a nitrogen atmosphere and the reaction mixture was then heated to 150 °C in an oil bath. Next, five times molar excess of phenyl isocyanate was added dropwise with a syringe through a rubber stopcock and stirred for 6 h by a magnetic bar under a nitrogen atmosphere. Upon cooling down, the reaction mixture was poured into ethanol. The precipitate was filtered and vacuum-dried at room temperature.

2.3. Synthesis of PDEF-b-PLA copolymers with chain extension reaction

PDEF was used as an initiator for the ring-opening polymerization (ROP) of lactide, resulting in the triblock PLA-PDEF-PLA diols. Subsequently, HDI was added to extend the PLA-PDEF-PLA chains (Scheme 1).

Initially, approximately 10 g of PDEF and varying amounts of LA were placed in a 100 ml flask equipped with a mechanical stirrer. The flask was purged with nitrogen gas three times and the reactants were dried for 3 h in a vacuum. During this period, a 0.1 g/ml toluene solution of $Sn(Oct)_2$, at 1 mol % relative to PDEF, was added. The reaction mixture was then heated to 160 °C in an oil bath and stirred for 4 h under a nitrogen atmosphere to facilitate the ring-opening polymerization. Following the reaction, the mixture was dissolved in chloroform and precipitated in methanol. The resulting precipitate was filtered and vacuum-dried at room temperature.

In the following step, the purified PLA-PDEF-PLA was dried for 3 h under a vacuum and then heated to 160 °C under a nitrogen atmosphere. 1.5 mol% HDI relative to PDEF was added dropwise under a nitrogen atmosphere and the mixture was stirred for an additional hour, during which a noticeable increase in viscosity was observed. After cooling the



Scheme 1. Synthesis scheme of PDEF-b-PLA copolymers.

mixture was again dissolved in chloroform and then precipitated in methanol. The final product was filtered and vacuum-dried at room temperature. PDEF was also chain-extended with the above-described method.

The PLA-PDEF-PLA diol obtained by ROP were denoted as $PDEF_x$-PLA_y (x: M_n of PDEF determined by GPC, y: M_n of PLA chain calculated from the ^{1}H NMR spectra), while the samples chain-extended with HDI were denoted as $PDEF_xPLA_y$_HDI.

2.4. *Fabrication of films*

The PDEF-PLA_HDI samples were heated and compressed using a manual hydraulic heating press (IMC- 180 C, Imoto Mfg. Co., Ltd., Kyoto, Japan) to produce a film. The sample (1.8–2 g) was sandwiched between aluminum plates set with 0.1 mm spacers. The press was heated to the target temperature and the sample was held for 5 min without pressure, then for 5 min at 10 MPa pressure. The pressing temperature for the PDEF-containing samples and the PLA sample was 140 and 190 °C respectively. The dimensions of the produced films were100 × 100 × 0.1 mm^3.

2.5. *Characterization*

The structure of each sample was analyzed by ^{1}H NMR measured with a JNM-ECS400 (400 Hz, JEOL, Tokyo, Japan) using deuterated chloroform with 0.05 vol % tetramethyl silane as the internal reference.

The molecular weights of the samples were determined by gel permeation chromatography on an HLC-8420GPC EcoSEC-Elite (Tosoh Co., Yamaguchi, Japan) instrument with a refractive index detector and TSKgel G3000HR column (Tosoh Co., Yamaguchi, Japan) with a size exclusion limit of 60,000 Da. The GPC test was carried out at a flow rate of 1.0 ml/min at 40 °C using chloroform as an eluent solvent, which was calibrated by polystyrene standards ($M_n = 5.89 \times 10^2$–3.79×10^4 g/mol).

Calorimetric analysis was carried out using a HITACHI DSC200 (Hitachi High-Tech Science Co., Tokyo, Japan) on 5–6 mg of samples. The thermal program was the following: (1) heating from 30 to 250 °C at 10 °C/min rate, (2) cooling from 250 to −50 °C at −10 °C/min rate, and (3) heating from −50 to 250 °C at 10 °C/min rate with constant nitrogen flow of 40 ml/min.

Thermogravimetric analysis was performed using HITACHI STA200RV (Hitachi High-Tech Science Co., Tokyo, Japan) on 5–6 mg of samples. The samples were heated from 40 to 600 °C at a 10 °C/min heating rate with a constant nitrogen flow of 100 ml/min.

The mechanical properties were measured using a Shimadzu EZ Graph (Shimadzu Corporation, Kyoto, Japan) instrument. The samples were cut from a film with a dumbbell-shaped cutter with the dimensions of 2.2 mm x 13 mm x 0.12–0.16 mm (width x length x thickness). The tensile test was performed at 20 mm/min speed in tensile mode with a 100 N tension load cell.

Optical transmittance was measured on films cut into rectangular shapes (1 cm x 3 cm) with a JASCO V-570 spectrophotometer (Jasco, Easton, MD, USA). Values of transmittance were acquired in the range of 200–800 nm with an acquisition speed of 400 nm/min and an excitation bandwidth of 1 nm.

The films' haze was measured through an NDH 4000 haze meter (Nippon Denshoku Industries Co., Ltd., Tokyo, Japan) at five different points.

The water contact angle of the film surface using around 1.0 μL droplets at room temperature was measured using a contact angle meter (DM300, Kyowa Interface Science Co. Ltd., Saitama, Japan). Images were captured after 10 seconds to reach a steady state.

3. Results and discussion

3.1. *Synthesis and characterization of PDEF*

PDEF was synthesized by two-step melt polycondensation, by mixing solid MFDC with a double excess DEG catalyzed by solid DBTO as presented in Scheme 1. When it comes to the preparation of FDCA-based polyesters, recrystallized MFDC was chosen for this synthesis as compared to FDCA, as it has higher purity and better solubility in DEG resulting in milder reaction temperatures compared to FDCA where reaction temperatures often varied between 180–240 °C [4,5,12,13,19–21]. In the transesterification step, the reactants were heated up to 160 °C to ensure the complete dissolution of MFDC in DEG, and it lasted 4 h in a nitrogen atmosphere to ensure the complete esterification of the methyl groups of MFDC. The reduction of pressure to <20 Pa immediately after transesterification resulted in the evaporation of the monomer with diethylene glycol. Therefore, during the polycondensation step, pressure was gradually reduced to ensure a controlled molecular weight increase and reproducibility and the removal of any low molecular weight side products and impurities gradually.

The chemical structure of PDEF was confirmed by ^{1}H NMR spectroscopy (400 MHz, $CDCl_3$): δ (ppm) = 3.60–3.65 ($\delta H_{c'}$, m, -O-**CH2**–CH2–OH), 3.70–3.75 ($\delta H_{b'}$, m, -CH2–**CH2**–OH), 3.8–3.9 (δH_c, t, –C(=O)-O-CH2–**CH2**–O–), 4.4–4.5 (δH_b, t, –C(=*O*)-O-**CH2**–CH2–O–), 7.1–7.2 (δH_a, m, **CH** in furan ring) (Fig. 1) [19,21]. The methyl group signal of MFDC around 4 ppm is absent suggesting full transesterification by DEG.

During the optimization of the PDEF synthesis, different molecular

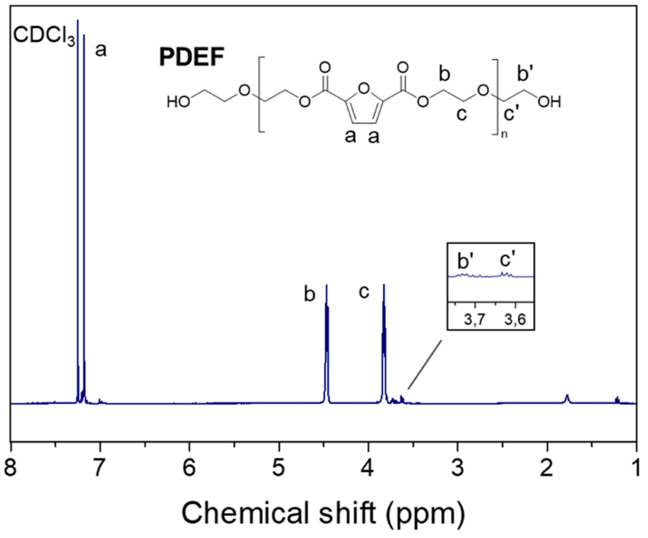


Fig. 1. ^{1}H NMR spectra of PDEF.

weights were achieved for 1, 4, and 8 h of polycondensation time (Table 1). The DSC thermograms showed an increase in T_g from 25.3 to 37.9 °C. Relatively low molecular weight PDEF oligomers with a T_g close to room temperature were achieved with 1-hour polycondensation time. However, the elutograms showed multiple peaks suggesting an insufficient time to achieve polymer chains with uniform molecular weight, which is preferred as an initiator. PDEF synthesized with 4-hour polycondensation time had an average M_n of 9600 g/mol with a single peak showing on the GPC elutograms and an average T_g of 33.8 °C which is above room temperature. Finally, M_n of 17,000 g/mol with 8-hour polycondensation time was achieved with the highest T_g, 37.9 °C.

To evaluate the ability of PDEF to initiate the ROP with lactide through the hydroxyl end-groups, PDEF was reacted with phenyl isocyanate in five times excess. The result of the end-capping was investigated by ^{1}H NMR (Fig. 2). The end-group methylene signals at 3.71 and 3.60 ppm reduced significantly in intensity as the hydroxyl group was replaced by the urethane bond. At the same time, a new peak appears at 7.35 ppm indicating the appearance of the benzene proton of the phenyl group, confirming the successful reaction between the terminal hydroxyl group and the isocyanate.

3.2. Synthesis and characterization of PDEF-b-PLA copolymers

A straightforward method to create alternating PLA block copolymers with a controlled structure is the ring-opening polymerization of lactide using a hydroxyl terminated comonomer as an initiator in the presence of a catalyst, usually $Sn(Oct)_2$ [22–27]. The ABA-type triblock copolymers can be chain-extended by isocyanates to yield alternating multiblock copolymers. In this case, PDEF synthesized with 4-hour polycondensation time has been chosen as the initiator as it is a good compromise between the uniform polydispersity compared to the 1-hour polycondensation samples, and the relatively low molecular weight compared to the 8-hour polycondensation sample for the effective initiation of the ring-opening of lactide.

After ring-opening polymerization, the structure of the PLA-PDEF-PLA copolymers was confirmed by ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 1.5–1.6 (δ$H_{e+e'}$, m, CH3 of the lactate units), 3.8–3.9 (δH_c, t, –C(=O)-O-CH2–**CH2**–O–), 4.4–4.5 (δH_b, t, –C(=O)-O-**CH2**–CH2–O–), 5.1–5.2 (δ$H_{d+d'}$, m, CH of the lactate units), 7.1–7.2 (δH_a, m, CH in furan ring) (Fig. 3).

The molecular weights of the PLA-PDEF-PLA triblock copolymers were evaluated by GPC while the length of the PLA segment was calculated from the ^{1}H NMR spectra along with the lactide conversion during ring-opening polymerization. The lactate/methylene unit ratios of the PLA-PDEF-PLA copolymers were determined from the integral ratios of the methylene signal in the PDEF segment and the lactate methine signal. From this ratio, the M_n of the PLA segment was defined as

$$M_{n,PLA} = M_{n,PDEF} \times \frac{72}{226} \times \left(\frac{lactate \times 2}{methylene}\right) \tag{1}$$

where $M_{n,PDEF}$ refers to the molecular weight of PDEF determined by GPC, 72 and 226 refers to the molecular weight of the repeating unit of PLA and PDEF respectively, *lactate* refers to the methine signal (δ 5.1–5.2 ppm) that includes a single proton, therefore a multiplier was included for the correct integral ratio, and *methylene* refers to the methylene signal in the PDEF segment (δ 4.4–4.5 ppm).

Table 1
Molecular weights, polydispersity, yield, and glass transition temperature (T_g) of the PDEF samples with different polycondensation times.

Sample name	Polycondensation time (hour)	M_n (g/mol)	M_w (g/mol)	PDI (M_w/M_n)	Yield (%)	T_g (°C)
PDEF12	1	5800	7400	1.3	50	29.0
PDEF17		5700	6400	1.1	43	25.3
PDEF2	4	9300	16,300	1.8	30	34.5
PDEF3		9300	15,400	1.7	34	33.3
PDEF5		11,000	20,000	1.8	58	32.4
PDEF13		7800	12,000	1.6	44	33.9
PDEF10		10,800	18,400	1.7	59	34.7
PDEF11	8	17,000	27,300	1.6	44	37.9

The lactide conversion was determined by the integral ratios of the PLA methine signal or methylene signal and the lactide methane signal or lactide methylene signal, expressed as

$$X_{LA} = \left(\frac{PLA}{PLA + lactide}\right) \times 100 \tag{2}$$

where *PLA* refers to the methine signal (δ 5.1–5.2 ppm) or methylene signal (δ 1.5–1.6 ppm) and *lactide* refers to the methine signal (δ 5.0–5.1 ppm) or methylene signal (δ 1.6–1.7 ppm).

The GPC results did not show a significant increase in molecular weight. Two different PLA chain lengths were achieved based on the calculation from the ^{1}H NMR spectra: 1170 and 340 g/mol, which is only 13–15 % of the theoretical feed amount of lactide. However, the LA conversion was above 80 % calculated from the ^{1}H NMR spectrum of purified samples. Therefore, the ROP might have been initiated by shorter fragments of PDEF or by other impurities. However, in these cases, the GPC elutograms showed one evenly distributed peak. Another explanation could be that the 160 °C reaction temperature limited the further evolution of the PLA chain resulting in a higher melting temperature of the copolymer.

The chain extension reaction was executed on the purified PLA-PDEF-PLA samples after ROP. HDI was added in a 1.5 mol excess compared to PDEF to avoid branching and M_n increased around two-fold after chain extension. In general, the high viscosity and elastic behavior of the melt samples made homogeneous mixing challenging, which might have resulted in insufficient mass transfer limiting the extent of chain extension (Table 2).

3.3. Thermal properties of the PDEF-b-PLA copolymers

The thermal properties were analyzed by DSC as shown in Fig. 4a and summarized in Table 3. In Table 3, the column marked "neat" is the homopolymer, the column marked "ROP" is the PLA-PDEF-PLA sample after ring-opening polymerization, while the column marked "CE" is the thermal properties of the PDEF-PLA_HDI sample after chain extension with HDI. The PDEF-PLA_HDI samples can be characterized exclusively by T_g suggesting a completely amorphous structure. PDEF used to initiate the ROP had a T_g slightly above room temperature, 34.5 °C for the PDEF9000PLA1000_HDI and 33.3 °C for the PDEF9000PLA300_HDI sample. After ROP, the T_g of the PLA-PDEF-PLA samples decreased by around 2 °C compared to PDEF, with no T_c and T_m detected. As the PLA segment length is estimated to be around 1000 and 300 g/mol, the formation of the crystal phase is challenging, moreover the regularity of the PDEF phase was disrupted resulting in a moderate decrease in T_g, thus the copolymer remained amorphous. After the chain extension reaction, T_g had increased by around 6 °C for both copolymers and by 7 °C for the chain-extended PDEF, exceeding both the T_g of neat PDEF and the PLA-PDEF-PLA samples due to the increased molecular weight. The commercial PLA sample had a T_c of 128.7 °C and T_m of 152.8 °C. The PDEF-PLA_HDI copolymers remained amorphous due to the disruption of regularity in the PDEF phase and the short PLA segment lengths, which prevent crystallization and therefore reduce the brittle nature of PLA. Chain extension effectively increased the molecular weight, leading to an increase in T_g.

The curves and the corresponding data for thermal stability are presented in Fig. 4b and Table 3. $T_{d,5}$ was highest for PLA, which could be attributed to the much larger molecular weight of commercial PLA, while $T_{d,5}$ of PDEF was lower by only 11 °C. The thermogravimetric curves of the PDEF-PLA samples show a similar curve to the

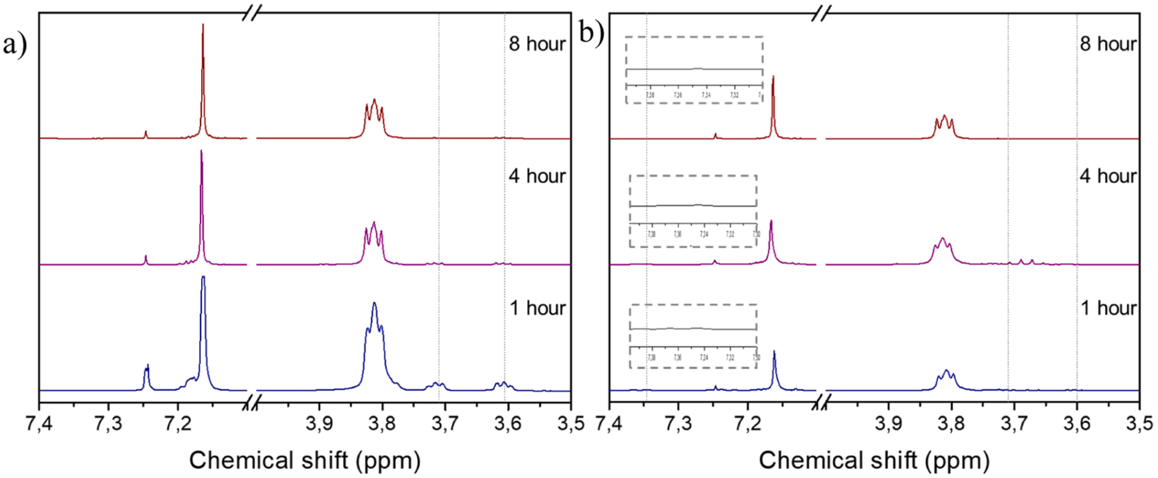


Fig. 2. ^{1}H NMR of PDEF synthesized with different polycondensation times a) before end-capping and b) after end-capping with phenyl isocyanate.

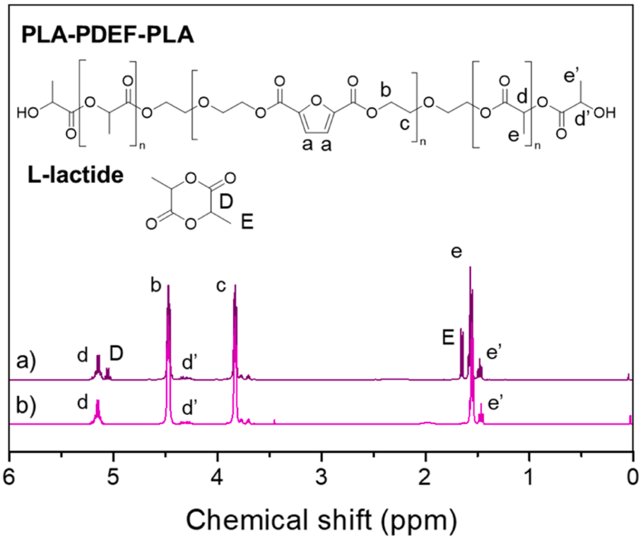


Fig. 3. ^{1}H NMR spectra of PLA-PDEF-PLA prepolymers a) batch sample b) purified sample.

homopolymer PDEF_HDI, with $T_{d,max}$ increased compared to PLA, $T_{d,5}$ was lower than both PLA and PDEF_HDI. While the homopolymers decompose in a single step, the copolymers show two distinct weight loss steps defined by the maximum decomposition rate: the one around 259–267 °C ($T_{d1,max}$) could be attributed to the weight loss of the PLA segment based on the lower $T_{d,max}$ of PLA compared to PDEF and as the ester bond is less stable than the ether bond. Meanwhile, the second weight loss step around 400 °C ($T_{d2,max}$) could be attributed to the decomposition of the PDEF segment. The char residue of PDEF-PLA_HDI and PDEF_HDI was between 6.9–8.4 %, significantly higher than the 1 % char residue for PLA. In general, copolymerization greatly improves the thermal stability of PLA as both $T_{d,max}$ and R_{600} values outperform the homopolymer.

3.4. *Mechanical properties of the films*

The mechanical properties of the PDEF-PLA films prepared by hot-press were assessed with the tensile test. The typical tensile curves are shown in Fig. 5. The Young's modulus, tensile stress at yield and break, and elongation at yield and break are summarized in Table 4. PLA showed a typical brittle failure with 40 MPa tensile strength and 20 % elongation at break. PDEF_HDI shows a much lower tensile stress at yield around 4.6 MPa with an elongation at break at around 600 % with a profile typical of thermoplastic elastomers. As for the copolymers, the tensile stress at yield and tensile stress at break were almost identical at 12 MPa, both between the homopolymer values while maintaining a Young's modulus above the mean average of the homopolymers. However, with decreasing PLA content the elongation at break increased significantly compared to PLA, by 700 % for PDEF9000PLA1000_HDI and by 1100 % for PDEF9000PLA300_HDI. Therefore, the incorporation of PDEF can reduce the brittle nature of PLA.

3.5. *Comparison with related work*

The obtained thermal and mechanical properties were compared with some similar works, where poly(alkoxy furanoates) were incorporated with PLA through different methods and concluded in Table 5. Rigotti et al. [12] prepared PPeF films by solvent casting from a chloroform solution of both components, while Fredi et al. [28] dissolved poly(hexamethylene-2,5-furanoate) and PLA in a mixture of chloroform and hexafluoroisopropanol (9:1 v/v). Long et al. [29] used a twin-screw compounder to prepare blends of PLA and PBF, while Bianchi et al. [30] prepared PLLA-PPeF by the chain extension of 50/50 wt % PLLA diol and PPeF with HDI. The compared samples all had a T_g above 50 °C due

Table 2
Characterization of the PLA-PDEF-PLA prepolymers after ring-opening polymerization (ROP) and PDEF-PLA_HDI copolymers and PDEF_HDI polymer after chain extension reaction (CE) with HDI.

Sample name	Initiator	Ring-opening polymerization (ROP)								Chain extension reaction (CE)		
	M_n (GPC) (g/mol)	M_n (GPC) (g/mol)	M_w (GPC) (g/mol)	PDI (GPC) (M_w/M_n)	PLA (theo.) (g/mol)	PLA (NMR) (g/mol)^1	LA conversion (NMR)^2	Yield (wt %)	[NCO]/[OH]	M_n (GPC) (g/mol)	M_w (GPC) (g/mol)	PDI (GPC) (M_w/M_n)
PDEF9000PLA1000_HDI	9200	9100	15,700	1.7	9000	1170	86	73	1.5	18,200	31,200	1.7
PDEF9000PLA300_HDI	9300	9100	14,700	1.6	2250	340	80	83	1.5	12,100	20,500	1.7
PDEF_HDI	5700	–	–	–	–	–	–	–	1.5	10,700	18,700	1.7

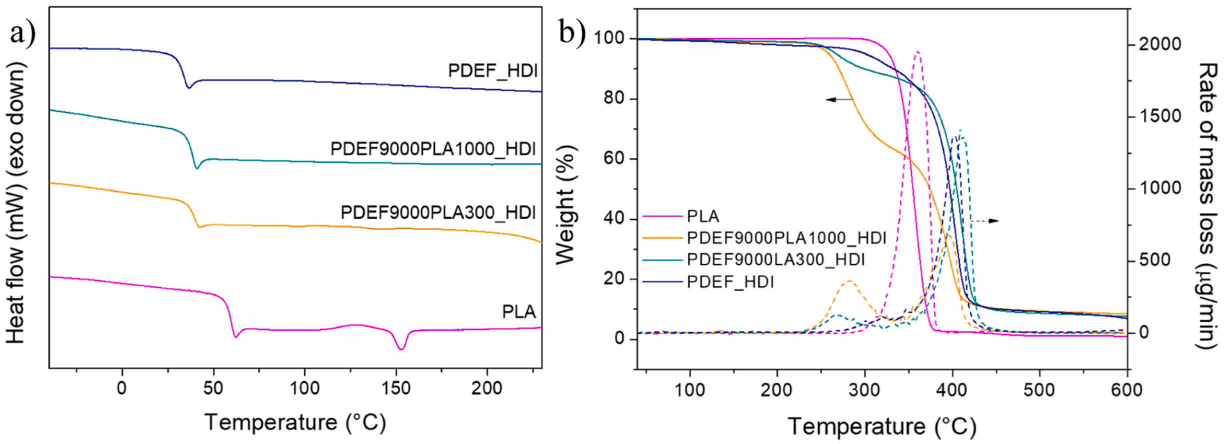


Fig. 4. a) DSC thermograms of the second heating scan and b) TGA thermograms of PDEF_HDI, PDEF-PLA_HDI copolymers, and PLA.

Table 3
Thermal properties and stability of the PDEF-PLA samples. Glass transition temperature (T_g), crystallization temperature (T_c), and melting temperature (T_m) were determined by DSC from the second heating scans for the neat materials, after the ring-opening reaction and after the chain extension reaction, where applicable. Decomposition temperature at 5 % weight loss of the initial weight ($T_{d,5}$), decomposition rate at which the local maximum rate occurred ($T_{d1,max}$,$T_{d2,max}$), and residual mass percentage at 600 °C ($R_{600\ °C}$) were determined by TGA.

Sample name	T_g (°C)			T_c (°C)			T_m (°C)			$T_{d,5}$ (°C)	$T_{d1,max}$ (°C)	$T_{d2,max}$ (°C)	$R_{600\ °C}$ (wt %)
	neat	ROP	CE	neat	ROP	CE	neat	ROP	CE				
PLA	58.8	–	–	128.7	–	–	152.8	–	–	327	361	–	1.0
PDEF9000PLA1000_HDI	34.5	32.8	38.5	–	–	–	–	–	–	259	281	397	8.4
PDEF9000PLA300_HDI	33.3	31.0	37.0	–	–	–	–	–	–	267	269	409	7.6
PDEF_HDI	25.3	–	32.2	–	–	–	–	–	–	301	–	402	6.9

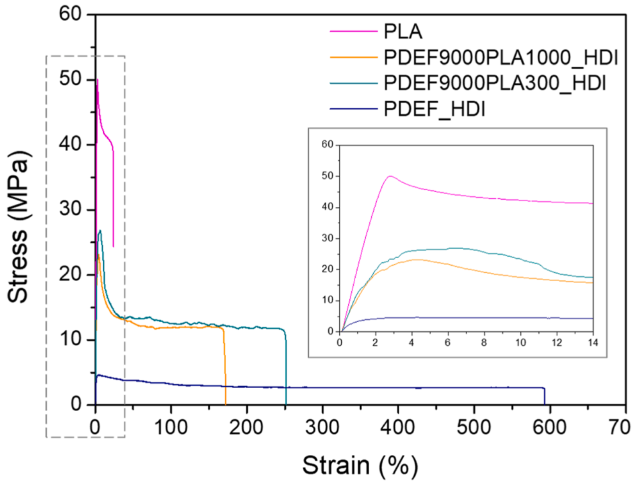


Fig. 5. Typical stress-strain curves of the PDEF_HDI, PDEF-PLA_HDI copolymers, and PLA films.

to their high PLA content, which was above 50 % for every sample except the chain-extended PLA-PPeF sample where the low molecular weight PLLA diol's molecular weight was not high enough to develop a crystalline domain similar to that observed in this work. As a result, every sample except the chain-extended PLLA-PPeF and this work did not exhibit T_{cc}, T_c or T_m. Data regarding thermal stability were only provided in two of the mentioned works. The $T_{d,5\ \%}$ was higher in both the butylene and pentamethylene samples, which is probably due to the high PLA content of the samples, as pure PLA has a higher $T_{d,5\ \%}$ than the poly(alkoxy furanoates). The $T_{d,max}$ was highest in this work, as the decomposition of the furanic moieties takes place at higher temperature compared to PLA. The elastic modulus for the PPeF containing samples was significantly lower than that of the ones in this work, while the poly (hexamethylene furanoate) had a comparable elastic modulus but a very rigid character. The PLA-PBF blends had a high modulus, tensile stress at yield, and elongation at break as well. In this case PBF successfully toughened PLA while it retained its high modulus, as pure PBF exhibits similar tensile properties to PDEF, with 1412 MPa Young's modulus, 32 MPa tensile strength at yield and 260 % elongation at break.

In conclusion, while PLA/pol(alkoxy furanoate)s haven't been obtained by direct copolymerization, the main challenge in drawing comparison is due to the different alkyl chain length and large gap in PLA content between the samples. In a related study by Quattrosoldi et al., the properties of PDEF were compared to pure PBF and PPeF, where PDEF outperformed both polymers in thermal stability. As for the mechanical properties, PDEF exhibited intermediate behavior between the rubbery, fully amorphous PPeF and semicrystalline PBF, as it undergoes yielding with a much higher elastic modulus than PPeF, but increased elongation at break compared to PBF. These findings are

Table 4
Mechanical properties of the PDEF_HDI, PDEF-PLA_HDI copolymers, and PLA films.

Sample name	Young's modulus [MPa]	Tensile stress at yield [MPa]	Elongation at yield [%]	Tensile stress at break [MPa]	Elongation at break [%]
PLA	2610 ± 161	53.1 ± 4.28	2.7 ± 0.06	39.5 ± 1.98	20.6 ± 7.25
PDEF9000PLA1000_HDI	1730 ± 118	24.3 ± 0.86	4.43 ± 0.63	12.1 ± 0.32	159 ± 38.4
PDEF9000PLA300_HDI	1410 ± 207	28.9 ± 4.06	6.30 ± 0.83	12.5 ± 1.77	255 ± 73.9
PDEF_HDI	690 ± 65	4.35 ± 0.49	4.34 ± 0.51	4.61 ± 0.91	575 ± 48.6

Table 5
Relevant thermal and mechanical properties taken from works that incorporate poly(alkoxy furanoates) with PLA.

Composition	Method	PLA content (wt %)	T_g (°C)	$T_{d,5\%}$ (°C)	$T_{d,max}$ (°C)	E (MPa)	Tensile stress at yield/break (MPa)	Tensile strain at break (%)	Reference
PLA/Poly(pentamethylene 2,5-furanoate)	Solvent casting from mixed solution	95	53	n.a.	n.a.	984	35.9/20.5	184	[12]
		80	54	n.a.	n.a.	880	29.2/19.4	126	
		70	13/56	n.a.	n.a.	764	25.7/20.2	202	
		50	13/55	n.a.	n.a.	389	12.4/11.0	33	
PLA/Poly(hexamethylene furanoate)	Solvent casting from mixed solution	70	53.6	n.a.	n.a.	1800	31/30	0.6	[28]
PLA/Poly(butylene 2,5-furan dicarboxylate)	Blending	95	60.0	316	365	3200	74.8/-	183.5	[29]
		90	60.4	312	368	3147	71.1/-	202.0	
		80	60.3	316	368	2661	64.1/-	223.0	
PLA/Poly(pentamethylene furanoate)	Chain.extension of PLLA and PPeF by HDI	50	22	282	308	535	n.a./10	162	[30]
PLA/Poly(diethylene furanoate)	ROP of LA by PDEF followed by chain extension by HDI	12	38.5	259	281/397	1730	24.3/12.1	159	This work
		4	37.0	267	269/409	1410	28.9/12.5	255	This work

similar to the conclusion of this study where the PDEF-b-PLA samples had the lowest T_g and highest $T_{d,max}$, while even at low PLA content they retained a high Young's modulus and tensile strength with high elongation at break.

3.6. Optical properties of the films

The transmittance curves for all samples are shown in Fig. 6a. PLA films have been widely considered in applications such as food packaging due to being bio-based and having good transparency. Neat PLA shows relatively good transparency, <20 % above 250 nm and around 40 % above 400 nm. However, it shows no UV transmission only in the UVC region, below 240 nm. On the contrary, PDEF has a strong UV-blocking effect as the transmittance below 300 nm is close to zero. This can be attributed to the good UV absorption behavior of the furan ring due to the presence of conjugated double bonds. PDEF had a 40–60 % transmittance in the visible region implying higher transparency than PLA. As for the PDEF-PLA_HDI samples, the UV-blocking effect was the same as the neat PDEF, however, the transmittance in the visible region was reduced to 8–28 % due to the phase separation of the different block

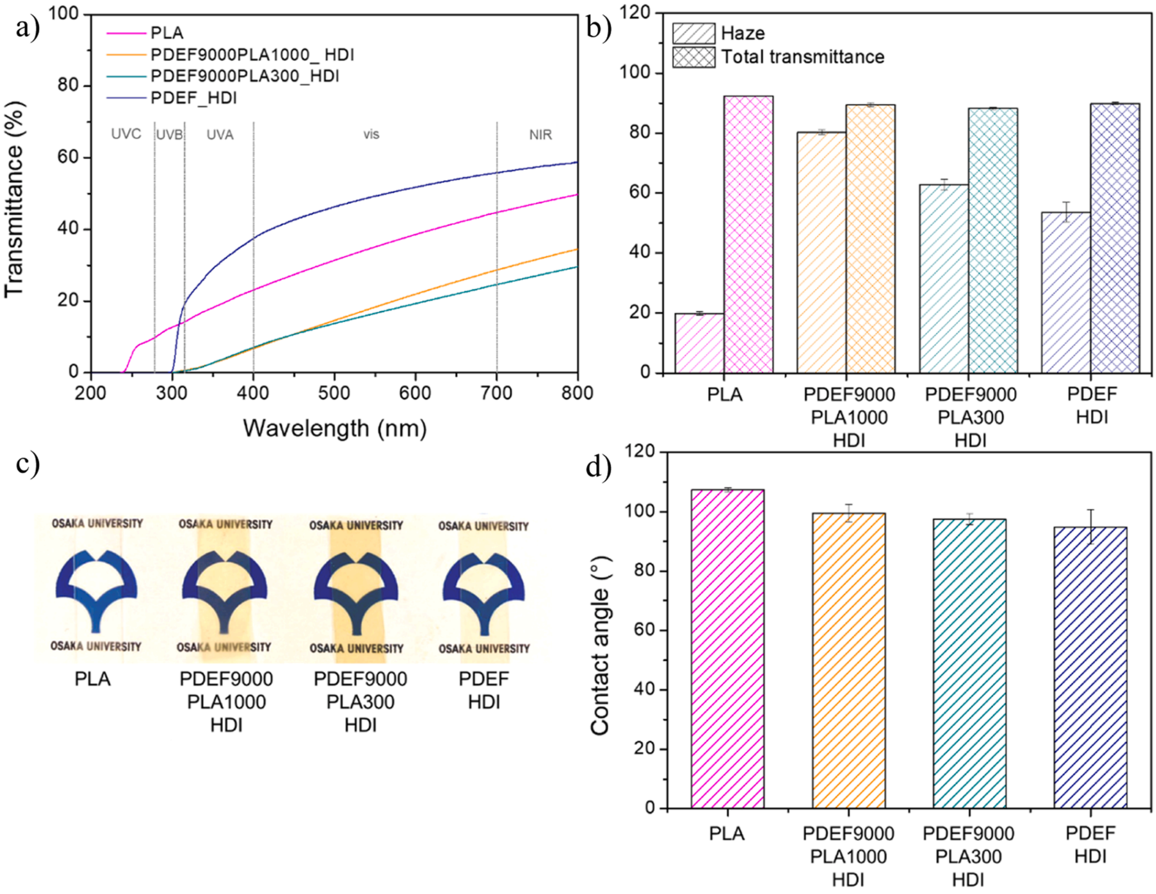


Fig. 6. a) UV–vis transmittance, b) haze results, c) water contact angle, d) digital images of the prepared PDEF_HDI, PDEF-PLA_HDI copolymers and PLA films.

segments, as immiscibility was also apparent in similar blends [12].

The haze and total transmittance of the films was measured as presented in Fig. 6b to gain information on the optical properties. PLA had the lowest haze at 20 %. The low haze was achieved by the rapid cooling of the film after hot-pressing, ensuring that the structure remained completely amorphous. The PDEF_HDI film had a much higher haze at 54 %. Even though the structure of the PDEF samples were also completely amorphous and the films appeared transparent, the significantly lower molecular weight of PDEF compared to PLA might have a great role in the higher haze. The PDEF-PLA_HDI copolymers showed a higher haze than PDEF, 80 % for the PDEF9000PLA1000_HDI and 63 % for the PDEF9000PLA300_HDI film respectively. This increase in haze could be explained by the increased degree of light scattering at the interfaces of the different block domains as in another study with PPeF-PLA solvent-cast films, the degree of phase separation grew rapidly with increasing PLA content, haze might increase with the increasing PLA content [12]. Despite the great variance of haze between the samples, the total transmittance was 92 % for PLA, and 88–90 % for all PDEF containing films. The films' obvious transparency can be seen in Fig. 6c. The PLA film had a clear white, and the PDEF-containing samples had a slightly yellow color of different degrees, which could indicate the UV-absorbing ability.

3.7. Wettability of the films

The wettability characterized by the water contact angle of the films is presented in Fig. 6d The PDEF film had a water contact angle of 95°, that showed a rather hydrophobic character. The copolymers show intermediate wettability, with increasing PLA chain length the water contact angle increased to 97° and 99.5° for PDEF9000PLA300_HDI and PDEF9000PLA1000_HDI respectively. Finally, PLA had the highest water contact angle at 107° While PLA has an ester bond in the repeating unit, each repeating unit in PDEF has an ether bond, two ester bonds through the carboxylic group, and the furanic oxygen, which can result in increased hydrogen bonding.

4. Conclusion

The purpose of this research was to synthesize an FDCA-based polyester, namely PDEF, to use as an initiator for the creation of bio-based PDEF-b-PLA alternating multiblock copolymers with improved optical, thermal and mechanical properties for film applications. PDEF with 9000 g/mol molecular weight was chosen to initiate the ROP of lactide, and the two copolymers had a length of 340 and 1170 g/mol, which was significantly lower than the theoretical chain length of 9000 and 2250 g/mol, despite the lactide conversion being over 80 %. The presence of hydroxyl end-groups in PDEF was confirmed with end-capping, therefore the evolution of the PLA chain length might have been limited by smaller fractions of PDEF or other impurities, or by the high viscosity of PDEF. T_g increased after the chain extension reaction by 4–7 °C for the PDEF-containing samples, while the temperature of maximum decomposition rate rate increased by 36 and 48 °C and the residual weight at 600 °C increased by 7.4 and 6.6 % for PDEF9000-PLA1000_HDI and PDEF9000PLA300_HDI respectively, compared to commercial PLA.

As PDEF showed the typical tensile curve of thermoplastic elastomers, the PDEF-PLA_HDI copolymers showed a great increase in elongation at break with a moderate decrease in Young's modulus and tensile stress at yield. All PDEF-containing samples had strong UV-blocking properties with a sharp cut-off at below 300 nm and total transmittance around 90 %. Typically, UV-blocking property is achieved by incorporating additives into the polymer matrix or as a coating, however, achieving uniform dispersion is challenging and affects the optical properties in the vis region as well as mechanical properties. Therefore, the design of polymer structures with UV-absorbing motifs is more favorable, in this case through the furan-containing moiety in the main chain. PDEF-b-PLA copolymers could be effective in applications where the polymer is constantly used in applications such as food packaging, photovoltaic cells, cable coating, or agricultural films, where the stability of the material is constantly threatened by exposure to UV radiation, while its rather hydrophobic character can also protect from moisture [31,32].

CRediT authorship contribution statement

Judit Rebeka Molnár: Writing – original draft, Visualization, Methodology, Investigation, Data curation, Conceptualization. **Yu-I Hsu:** Writing – review & editing, Visualization, Methodology, Funding acquisition, Conceptualization. **Hiroshi Uyama:** Supervision, Project administration, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

This work was supported by Japan Science and Technology Agency (JST) PRESTO Grant Number JPMJPR23N4, the Environment Research and Technology Development Fund JPMEERF21S11900 of the Environmental Restoration and Conservation Agency of Japan, and Japan Society for the Promotion of Science (JSPS) KAKENHI Grants (22K21348 and 23K26717). The first author would like to express her gratitude for the support of the Japanese Government (MEXT) Scholarship funded by the Ministry of Education, Culture, Sports, Science and Technology.

Data availability

No data was used for the research described in the article.

References

[1] E. Jong, H.A. de Visser, A.S. Dias, C. Harvey, G.J.M. Gruter, The road to bring FDCA and PEF to the market, Polymers (Basel) 14 (2022), https://doi.org/10.3390/polym14050943.

[2] S. Prasad, A.J. Khalid, V. Narishetty, V. Kumar, S. Dutta, E. Ahmad, Recent advances in the production of 2,5-furandicarboxylic acid from biorenewable resources, Mater. Sci. Energy Technol. 6 (2023) 502–521, https://doi.org/10.1016/j.mset.2023.04.005.

[3] J.G. Rosenboom, D.K. Hohl, P. Fleckenstein, G. Storti, M. Morbidelli, Bottle-grade polyethylene furanoate from ring-opening polymerisation of cyclic oligomers, Nat. Commun. 9 (1) (2018), https://doi.org/10.1038/s41467-018-05147-y.

[4] H. Hu, R. Zhang, W.B. Ying, Z. Kong, K. Wang, J. Wang, J. Zhu, Biodegradable elastomer from 2,5-furandicarboxylic acid and ϵ-caprolactone: effect of crystallization on elasticity, ACS Sustain. Chem. Eng. 7 (21) (2019) 17778–17788, https://doi.org/10.1021/acssuschemeng.9b04210.

[5] J. Wang, X. Zhang, X. Fei, R. Gao, F. Liu, L. Fan, J. Zhu, X. Liu, Synthesis of high thermal-resistant poly(Ester-Ether) elastomers from Bio-based 2,5-furandicarboxylic acid, ACS Sustain. Chem. Eng. 10 (41) (2022) 13595–13606, https://doi.org/10.1021/acssuschemeng.2c02751.

[6] M. Rhein, A. Demharter, B. Felker, M.A.R. Meier, A fully biobased aromatic polyester polyol for polyisocyanurate rigid foams: poly(Diethylene Furanoate), ACS Appl. Polym. Mater. 4 (9) (2022) 6514–6520, https://doi.org/10.1021/acsapm.2c00922.

[7] X. Fei, X. Zhang, J. Liu, J. Wang, X. Liu, Synthesis of a fire-retardant and high tg biobased polyester from 2,5-furandicarboxylic acid, Polym. J. 54 (8) (2022) 995–1008, https://doi.org/10.1038/s41428-022-00642-y.

[8] J. Ding, J. Wang, W. Cao, H. Zheng, Z. Guo, Z. Fang, P. Chen, J. Li, Flame retarding and strengthening poly(Ethylene 2,5-Furandicarboxylate-Co-Ethylene Terephthalate) using phosphonate containing genistein, ACS Sustain. Chem. Eng. 11 (16) (2023) 6416–6426, https://doi.org/10.1021/acssuschemeng.3c00333.

[9] N. Yoshie, S. Yoshida, K. Matsuoka, Self-healing of biobased furan polymers: recovery of high mechanical strength by mild heating, Polym. Degrad. Stab. 161 (2019) 13–18, https://doi.org/10.1016/j.polymdegradstab.2019.01.007.

[10] E. Gubbels, L. Jasinska-Walc, B.A.J. Noordover, C.E. Koning, Linear and branched polyester resins based on dimethyl-2,5- furandicarboxylate for coating

applications, Eur. Polym. J. 49 (10) (2013) 3188–3198, https://doi.org/10.1016/j.eurpolymj.2013.06.019.

[11] H. Xie, L. Wu, B.G. Li, P. Dubois, Biobased poly(Ethylene- Co-Hexamethylene 2,5-Furandicarboxylate) (PEHF) copolyesters with superior tensile properties, Ind. Eng. Chem. Res. 57 (39) (2018) 13094–13102, https://doi.org/10.1021/acs.iecr.8b03204.

[12] D. Rigotti, M. Soccio, A. Dorigato, M. Gazzano, V. Siracusa, G. Fredi, N. Lotti, Novel biobased polylactic acid/poly(Pentamethylene 2,5-Furanoate) blends for sustainable food packaging, ACS Sustain. Chem. Eng. 9 (41) (2021) 13742–13750, https://doi.org/10.1021/acssuschemeng.1c04092.

[13] Z. Terzopoulou, A. Zamboulis, L. Papadopoulos, M.E. Grigora, K. Tsongas, D. Tzetzis, D.N. Bikiaris, G.Z. Papageorgiou, Blending PLA with polyesters based on 2,5-furan dicarboxylic acid: evaluation of physicochemical and nanomechanical properties, Polymers (Basel) 14 (21) (2022), https://doi.org/10.3390/polym14214725.

[14] H. Xu, J. Zhou, K. Odelius, Z. Guo, X. Guan, M. Hakkarainen, Nanostructured phase morphology of a biobased copolymer for tough and UV-resistant polylactide, ACS Appl. Polym. Mater. 3 (4) (2021) 1973–1982, https://doi.org/10.1021/acsapm.1c00057.

[15] D. Sun, J. Mo, W. Liu, N. Yan, X. Qiu, Ultra-strong and tough bio-based polyester elastomer with excellent photothermal shape memory effect and degradation performance, Adv. Funct. Mater. 34 (39) (2024), https://doi.org/10.1002/adfm.202403333.

[16] A.M. Ahmed, T.P. Kainulainen, J.P. Heiskanen, Furfural-based modification of PET for UV-blocking copolymers with decreased oxygen permeability, Ind. Eng. Chem. Res. 60 (19) (2021) 7495–7504, https://doi.org/10.1021/acs.iecr.1c00629.

[17] T.P. Kainulainen, T.A.O. Parviainen, J.A. Sirviö, L.J.R. McGeachie, J.P. Heiskanen, High oxygen barrier polyester from 3,3′-bifuran-5,5′-dicarboxylic acid, ACS Macro Lett (2023) 147–151, https://doi.org/10.1021/acsmacrolett.2c00743.

[18] G.Z. Papageorgiou, V. Tsanaktsis, D.N. Bikiaris, Synthesis of poly(Ethylene Furandicarboxylate) polyester using monomers derived from renewable resources: thermal behavior comparison with PET and PEN, Phys. Chem. Chem. Phys. 16 (17) (2014) 7946–7958, https://doi.org/10.1039/c4cp00518j.

[19] S. Tian, X. Cao, K. Luo, Y. Lin, W. Wang, J. Xu, B. Guo, Effects of nonhydroxyl oxygen heteroatoms in diethylene glycols on the properties of 2,5-furandicarboxylic acid-based polyesters, Biomacromolecules 22 (11) (2021) 4823–4832, https://doi.org/10.1021/acs.biomac.1c01106.

[20] L. Papadopoulos, A. Zamboulis, N. Kasmi, M. Wahbi, C. Nannou, D. A. Lambropoulou, M. Kostoglou, G.Z. Papageorgiou, D.N. Bikiaris, Investigation of the catalytic activity and reaction kinetic modeling of two antimony catalysts in the synthesis of poly(Ethylene Furanoate), Green Chem 23 (6) (2021) 2507–2524, https://doi.org/10.1039/d0gc04254d.

[21] H. Meng, Z. Li, L. Wu, B.G. Li, Y. Hu, K. Wang, Synthesis and properties of poly (Ethylene-Co-Diethylene Glycol 2,5-Furandicarboxylate) copolymers, J. Appl. Polym. Sci. 139 (15) (2022), https://doi.org/10.1002/app.51921.

[22] Y.I. Hsu, K. Masutani, T. Yamaoka, Y. Kimura, Tuning of sol-gel transition in the mixed polymer micelle solutions of copolymer mixtures consisting of enantiomeric diblock and triblock copolymers of polylactide and poly(Ethylene Glycol), Macromol. Chem. Phys. 216 (8) (2015) 837–846, https://doi.org/10.1002/macp.201400581.

[23] A. Takagi, Y.I. Hsu, H. Uyama, Biodegradable poly(Lactic Acid) and polycaprolactone alternating multiblock copolymers with controllable mechanical properties, Polym. Degrad. Stab. 218 (2023), https://doi.org/10.1016/j.polymdegradstab.2023.110564.

[24] C.W. Lee, T. Manoshiro, Y.I. Hsu, Y. Kimura, Gelation behavior of bioabsorbable hydrogels consisting of enantiomeric mixtures of A-B-A tri-block copolymers of polylactides (A) and poly(Ethylene Glycol) (B), Macromol. Chem. Phys. 213 (20) (2012) 2174–2180, https://doi.org/10.1002/macp.201200375.

[25] S. Kaihara, S. Matsumura, A.G. Mikos, J.P. Fisher, Synthesis of poly(L-Lactide) and polyglycolide by ring-opening polymerization, Nat. Protoc. 2 (11) (2007) 2667–2671, https://doi.org/10.1038/nprot.2007.391.

[26] T. Fujiwara, T. Mukose, T. Yamaoka, H. Yamane, S. Sakurai, Y. Kimura, Novel thermo-responsive formation of a hydrogel by stereo-complexation between PLLA-PEG-PLLa and PDLA-PEG-PDLA block copolymers, Macromol. Biosci. 1 (5) (2001) 204–208, https://doi.org/10.1002/1616-5195(20010701)1:5<204::AID−MABI204>3.0.CO;2-H.

[27] M. He, Y.I. Hsu, H. Uyama, Design of novel poly(L-Lactide)-based shape memory multiblock copolymers for biodegradable esophageal stent application, Appl. Mater. Today 36 (2024), https://doi.org/10.1016/j.apmt.2024.102057.

[28] Fredi, G. Tuning thermo-mechanical properties of poly(Lactic Acid) films through blending with bioderived poly(Alkylene Furanoate)s with different alkyl chain length for sustainable packaging. 2021.

[29] Y. Long, R. Zhang, J. Huang, J. Wang, Y. Jiang, G. Hu, J. Yang, J. Zhu, Tensile property balanced and gas barrier improved poly(Lactic Acid) by blending with biobased poly(Butylene 2,5-Furan Dicarboxylate), ACS Sustain. Chem. Eng. 5 (10) (2017) 9244–9253, https://doi.org/10.1021/acssuschemeng.7b02196.

[30] E. Bianchi, G. Guidotti, M. Soccio, V. Siracusa, M. Gazzano, E. Salatelli, N. Lotti, Biobased and compostable multiblock copolymer of poly(l-Lactic Acid) containing 2,5-furandicarboxylic acid for sustainable food packaging: the role of parent homopolymers in the composting kinetics and mechanism, Biomacromolecules 24 (5) (2023) 2356–2368, https://doi.org/10.1021/acs.biomac.3c00216.

[31] T.P. Kainulainen, J.A. Sirviö, J. Sethi, T.I. Hukka, J.P. Heiskanen, UV-blocking synthetic biopolymer from biomass-based bifuran diester and ethylene glycol, Macromolecules 51 (5) (2018) 1822–1829, https://doi.org/10.1021/acs.macromol.7b02457.

[32] H. Zhang, X. Cheng, C. Liu, Z. Liu, L. Liu, C. Feng, J. Ju, X. Yao, Ultraviolet-blocking polymers and composites: recent advances and future perspectives, J. Mater. Chem. A 12 (47) (2024) 32638–32664, https://doi.org/10.1039/D4TA06335J.