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Novel biobased poly(trimethylene 2,5-furanoate-co-trimethylene dodecanedioate) PTFcoDod copolymers for sustainable packaging

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ABSTRACT

New biobased aliphatic-aromatic flexible copolymers based on 2,5-furandicarboxylic acid, 1,3-propanediol and long aliphatic dicarboxylic acid (dodecanedioic acid) were synthesized by melt polycondensation. The structure of poly(trimethylene 2,5-furanoate-co-trimethylene dodecanedioate) (PTFcoDod), as well as their thermal, mechanical and barrier properties were examined. Selected copolymers were also tested for thermally induced shape memory properties. Gas barrier tests displayed that the prepared copolymers had satisfactory barrier properties, comparable or even better than polymers like PET, PLA and PBAT. Tensile testing confirmed the excellent mechanical properties of PTFcoDod films that, depending on the composition, are characterized by either high tensile strength and stiffness or great flexibility, with an elongation at break exceeding 300 %. Last, lab-scale degradation tests in compost showed that the PTFcoDod copolymers were biodegradable, with a rate in line with their composition. The obtained results are a continuation of research on bio-based random aliphatic-aromatic copolymers and indicate the wide potential of the obtained materials, especially for applications as both rigid and flexible environmentally friendly packaging.

1. Introduction

The food packaging industry accounts for over 43 % of the global plastics market (Bulk Chemicals, 2023). Polymers characterized by low permeability to gases are particularly useful in this field, as they ensure a long shelf life of stored products and allow to reduce wastes. To obtain low barrier properties, multi-layer materials, such as those containing EVOH, are often used. However, this kind of package possesses some drawbacks which include higher production costs and difficult recycling (Barlow and Morgan, 2013). Currently, great emphasis is placed on the ecological aspect of polymers. Indeed, the use of biodegradable and bio-based materials in the packaging industry would not only reduce petroleum consumption and decrease greenhouse gases emissions but would also contribute to sustainable waste management. Data for 2023 shows that currently, approximately 0.5 % of produced plastics are biopolymers (European Bioplastics, 2023). However, this number increases from year to year, and their production capacity is expected to reach about 7 million tons in 2028.

An outstanding monomer for the synthesis of bio-based polymers, whose potential has already been proven, is 2,5-furandicarboxylic acid (FDCA) (Hwang et al., 2023; Marshall et al., 2022; Terzopoulou et al., 2020). In particular, the FDCA-based poly(trimethylene furanoate) (PTF) is characterized by high barrier properties, exhibiting 16 times lower O_2 permeability and over 47 times lower CO_2 permeability than PET. However, this homopolymer is not biodegradable, and its application possibilities are additionally limited by its high stiffness (Guidotti et al., 2020; Quattrosoldi et al., 2022). Currently, flexible packaging dominates the plastic packaging market (Meena et al., 2017), due to the increasing demand for lightweight and cheaper solutions, together with the rising awareness towards the preservation of sources, keeping at the same time the performances of the material and even improving the shelf life of the packaged goods. Therefore, in order to modify the

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mechanical properties and increase the biodegradability of PTF, deep research has been undertaken on PTF-based copolymers.

Numerous research works are currently underway to improve the ductility and processability of PTF keeping on the same or improved level gas barrier properties to extend its applications for food packaging and disposable articles. Examples of PTF modification include copolymerization with cyclic aliphatic diol 2,2,4,4-tetramethyl-1,3-cyclobutanediol (CBDO), which at the level of 10 and 18 mol% of this co-unit demonstrated better barrier properties, increased T_g and better mechanical properties (Wang et al., 2017b) but it is not biodegradable material. It was shown also that due to the large carboxyl intercalation angle and the weaker electronegativity of the sulfur atoms in the thiophene ring in comparison to furane ring, the stiffness of PTF can be reduced and Tg decrease by introducing 2,5-thiophenedicarboxylic acid (Wang, Dong, 2024). Additionally, modifications of PTF by copolymerization include also search paths to make them a sustainable choice for easily recyclable or compostable packaging. To our knowledge, there are still no studies on the biodegradability of PTF under realistic natural conditions. Our recent study showed that PTF can be chemically recycled (Agostinho et al., 2025), but this process is costly. As well we demonstrated in our previous work that PTF is more susceptible to (bio) degradation during composting, its films at 58 ∘C with 99 % relative humidity, revealing no significant polymer weight loss after 6 months (ca. 2 %), but the molecular weight decreased approximately 30 % (Zubkiewicz et al., 2022). This study demonstrates that PTF can be more susceptible to (bio)degradation than its fossil-based counterparts [Chen et al., (2020), Paszkiewicz et al., (2022)].

As a sustainable industrial process, the biotransformation of dicarboxylic acids (DCAs) from fatty acids and alkanes by microorganisms has continuously garnered interest, since synthesis via chemical oxidation causes problems in terms of the environment and safety (Cao et al., 2017, 2018; Buathong et al., 2020, 2019; Wonoputri et al., 2020). Recently, a new platform for production of ω-hydroxydodecanoic acid (HDA) by engineering the yeast *Candida viswanathii* that converts dodecane into dodecanedioic acid (DodA), with HDA as a metabolic intermediate was developed (Chang et al., 2025).

In our previous works, we investigated random copolymers based on 2,5-furanedicarboxylic acid and aliphatic dicarboxylic acids containing 6 and 8 methylene groups in the main chain (suberic acid and sebacic acid, respectively) (Zubkiewicz et al., 2025, 2022, 2025). The tested copolymers were characterized by exceptional barrier properties, as the gas transition rate (GTR) values of the copolymers containing 15 mol% of co-unit were comparable to those of EVOH. Moreover, the investigated materials underwent expedited biodegradation in compost by increasing the content of aliphatic co-units, the richest copolymeric compositions degrading up to 100 % after less than 6 months (Zubkiewicz et al., 2022, 2025). Due to these unique properties, it was decided to synthesize and characterize new copolyesters based on PTF and a different dicarboxylic acid, containing a longer aliphatic chain. Extending this strategy to longer aliphatic chains, dodecanedioic acid emerges as a promising comonomer. Indeed, a longer linear chain may contribute not only to faster biodegradation, but also to better mechanical elasticity, maintaining at the same time good barrier properties. Therefore, in this paper, poly(trimethylene 2,5-furanoate-co-trimethylene dodecanedioate) (PTFcoDod) copolymers were investigated for potential applications in the field of food packaging.

2. Materials and methods

2.1. Synthesis of polymers

The synthesis of PTFcoDod copolymers was carried out in a 1000 cm^3 steel reactor (Autoclave Engineers, Pennsylvania, USA), according to the procedure described in previous works (Paszkiewicz et al., 2022; Zubkiewicz et al., 2021). In the first stage, 2,5-furandicarboxylic acid dimethyl ester (DMFDCA, > 99.8 %, Matrix Fine Chemicals GmbH, Switzerland), 1,3-propanediol (PDO, > 99 %, DuPont Tate & Lyle Bio-Products, Loudon, USA), tetrabutyl orthotitanate catalyst (TBT, > 97 %, Fluka Chemie AG, Buchs, Switzerland), and dimethyl dodecanedioate (DMDod, > 99 %, Career Henan Chemical Co., China) were charged into the reactor. The transesterification reaction took place at a temperature of 160–165 °C. The course of the reaction was monitored by observing the amount of methanol distilled off. When the first step was completed, the appropriate amount of the second part of the catalyst (TBT) was added to the reactor. The second stage of synthesis (polycondensation reaction) took place at a temperature of 235 °C and under reduced pressure of ~20 Pa. The progress of the reaction was monitored by observing the increase in the torque value. The reaction was completed when the mixture reached the desired high viscosity. The obtained copolymers were then extruded from the reactor under nitrogen flow, cooled in water bath and granulated.

2.2. Sample preparation

Samples used for the testing of mechanical properties, shape memory behavior and barrier properties, as well as for degradation tests were prepared in the form of films using a Collin P200P press. The pressing temperature of each material was 20 °C higher than the corresponding melting temperature, this last determined by calorimetric measurements. Each material was placed between two Kapton or Teflon layers. Samples for mechanical and barrier tests were prepared in the form of films with a thickness of 100 ± 10 μm and a diameter of 11 cm. The pressure and time of individual stages were respectively: 5 bars for 180 s (preliminary pressing), 240 bar for 120 s (proper pressing), 120 bar for 45 s (cooling). The obtained films were cut, depending on their purpose, into strips 2 cm× 12 cm (mechanical properties tests), 0.7 cm× 3 cm (shape memory tests), or into squares of 2 cm sides (degradation tests).

2.3. Characterization of materials

^{1}H NMR spectra were obtained using a Bruker spectrometer operating at a frequency of 400 MHz. The solvent was $CDCl_3$ for the copolymers or a mixture of $CDCl_3/CF_3COOD$ (10:1 v/v) in the case of PTF homopolymer. Tetramethylsilane (TMS) was used as a standard for chemical shift calibration. The equations used to calculate the degrees of randomness, molar fractions of TDod co-unit and the length of TF and TDod sequences are presented in the Supplementary Information (SI) (Eq. 1–4S).

SEC measurements were determined using a Waters GPC instrument equipped with a Waters 1515 isocratic pump, a Waters 2414 refractive index detector (at 35 °C), a Waters 2707 autosampler, a PSS PFG guard column, and two columns arranged in series (7 μm, 8 × 300 mm). Measurements were performed in 1,1,1,3,3,3-hexafluoroisopropanol (HFIP) at 40 °C with a flow rate of 0.8 ml/min. Poly(methyl methacrylate) (Polymer Laboratories) ranging from 580 to 7.1×10^6 g mol^{-1} was used as standard.

DSC measurements were performed using a F1 Phoenix (Netzsch, Selb, Germany) calorimeter. Samples weighing approximately 10 mg were subjected to repeated heating-cooling cycles under nitrogen flow (20 ml/min) in the temperature range –60–200 °C, at heating and cooling rates of 10, 5, 3 and 1 °C/min, respectively.

XRD analysis was performed using X'Pert PRO PANalytical diffractometer operating with Cu Ka radiation ($\lambda = 0.154$ nm), at 40 kV and 30 mA over the 2θ range from 4 to 60° with a step of 0.02°.

Thermal and thermo-oxidative stability was tested using a TGA 92–16.18 SETARAM thermogravimeter (Caluire-et-Cuire, France). The tests were carried out under inert atmosphere (argon) and under oxidizing atmosphere (dry, synthetic air: N_2:O_2 = 80:20 vol%), with a gas flow of 20 ml/min and a heating rate of 10 °C/min in the temperature range from 20 °C to 700 °C.

The water contact angle (WCA) was measured on polymeric flat films which were previously cleaned with ethanol and dried at room temperature. Measurements were made using a KSVCAM101Instrument. The wetting angle was measured 1 s after 4 μL of distilled water droplet was dropped by syringe needle on the polymer surface. The results are given as the average value of 8 drops that were placed in different positions on two films.

Mechanical properties were tested on the Autograph AG-X plus universal testing machine (Shimadzu, Germany) equipped with an optical extensometer, 1 kN Shimadzu load cell and TRAPEZIUM X software. Measurements were performed at room temperature in accordance with the PN-EN ISO 527 standard. The reported values are an average of six test specimens extended at a rate of 5 mm/min.

The thermally induced shape memory effect for selected copolymeric compositions was investigated using a dynamic thermomechanical analyzer (DMA Q800, TA Instruments). Before testing, foil samples were stabilized at 50 °C for 24 h. The cycles consisting of heating - stress loading - cooling - stress unloading - heating were conducted, with constant heating and cooling rate of 10 °C/min. The temperature at which the samples were stretched depended on the T_g value of the material and fixing of temporary shape was performed at a temperature of 0 °C. The details of the procedure are described in previous papers (Irska et al., 2020; Paszkiewicz et al., 2021; Zubkiewicz et al., 2022).

Gas barrier properties were tested using the GDP-C gas permeability testing apparatus (Brugger Feinmechanik GmbH) in accordance with the ASTM 1434–82, DIN 53536 and ISO/DIS 15105–1 standards. Samples were tested at a temperature of 23 °C and relative humidity RH = 0 %, with an O_2 or CO_2 flow rate of 100 $cm^3 min^{-1}$. The obtained gas transmission rate (GTR) values were given as an average of 3 measurements.

Biodegradation tests were carried out on a laboratory scale using compost provided by HerAmbiente S.p.A. (Bologna, Italy). Composting of the copolymers was carried out at a temperature of 58 ± 0.1°C and a relative humidity of 99 %. Before placing in the compost (pH ~ 8), film samples were washed with a 70 vol% ethanol solution and distilled water, then dried and weighed. After appropriate timepoints (1, 2, 3, 4, 5, 6 months), 2 samples of each material were removed, washed with a 70 % ethanol solution and distilled water, dried and then weighed. The result reported has been calculated as the average mass loss for two samples. Moreover, the main thermal transitions of the partially degraded samples were analyzed by DSC.

3. Results

3.1. Chemical characterization of PTF and PTFcoDod copolymers

The chemical structure of PTFcoDod copolymers was confirmed by ^{1}H NMR and FTIR spectroscopy analysis. The obtained spectra are shown in Figs. 1S and 2S, respectively, together with the peaks' attribution. The actual molar fraction of TDod co-units (Table 1), calculated on the basis of ^{1}H NMR spectra, are close to the theoretical values, suggesting a good control over the polymerization process. As expected, by increasing the content of aliphatic co-units, the length of the TF sequences decreased, while the length of the TDod sequences increased. The degree of randomness (R) is close to 1 in all cases (Table 1), which means that the molecular architecture of the synthesized PTFcoDod copolymers can be considered as random. The information obtained from ^{1}H NMR (Fig. 1S, Table 1) and FTIR analyses (Fig. 2S, Table 1S)

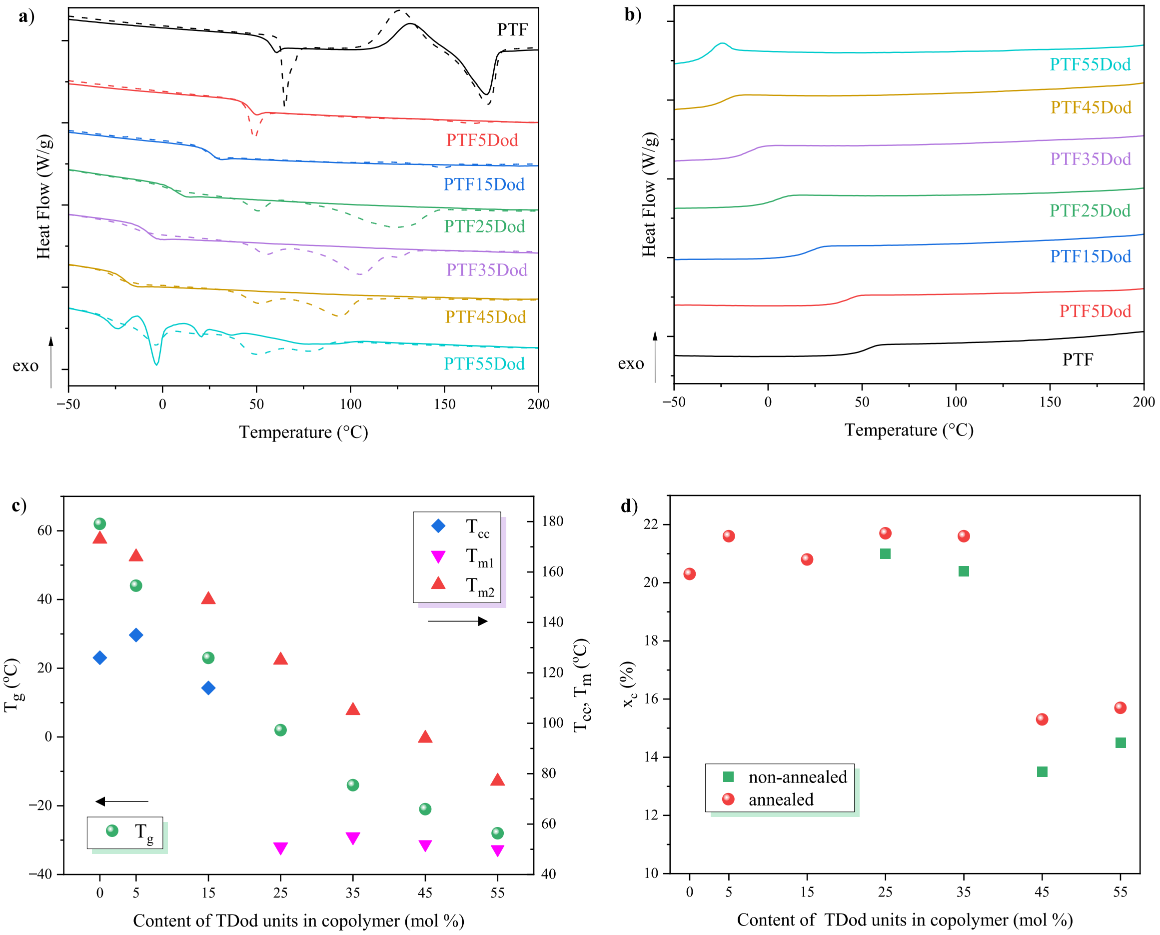

Fig. 1. DSC heating (a) and cooling (b) thermograms at rate of 10 ℃ min^{-1} for PTF and PTFcoDod (the dashed lines represent the first heating scans), dependence of T_g, T_{cc} and T_m on the PTFcoDod copolymer composition (c) and degree of crystallinity determined from XRD patterns(d).

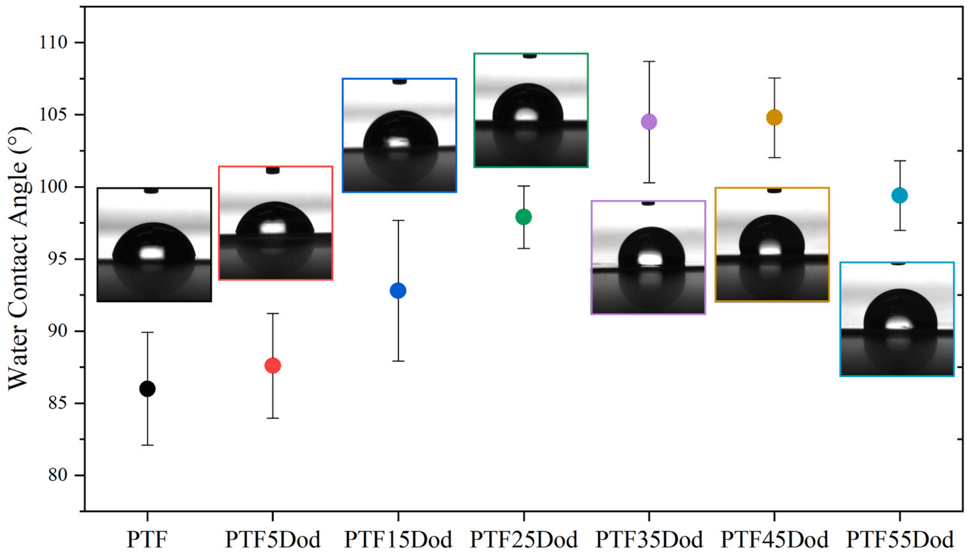

Fig. 2. Water contact angle of PTF and PTFcoDod copolymers.

Table 1
Molecular characterization data of PTF and PTFcoDod copolymers.

Sample	Feed φ^{A}_{TDod} (mol%)	^{1}H NMR φ^{B}_{TDod} (mol%)	$L_{n,TF}$	$L_{n,TDod}$	R	SEC M_n (g mol^{-1})	M_w (g mol^{-1})	PDI
PTF	0	0	-	-	-	37 100	84 400	2.27
PTF5Dod	5	5.93	5.53	1.20	1.01	40 100	90 200	2.25
PTF15Dod	15	14.18	4.33	1.17	1.09	41 000	96 300	2.34
PTF25Dod	25	24.43	2.65	1.41	1.09	39 400	98 800	2.51
PTF35Dod	35	34.05	2.35	1.51	1.09	42 900	110 300	2.57
PTF45Dod	45	43.11	2.01	1.76	1.07	43 600	113 300	2.60
PTF55Dod	55	54.92	1.67	1.89	1.12	38 000	82 000	2.16

φ^{A}_{TDod} – theoretical molar fraction of TDod in copolymer, φ^{B}_{TDod} - molar fraction of TDod in copolymer determined by ^{1}H NMR; R - degree of randomness of copolymers; $L_{n,TF}$ and $L_{n,TDod}$ represent the sequence length of trimethylene furanoate (TF) and trimethylene dodecanedioate (TDod) units, respectively; M_n, M_w – average number and weight molecular weight, respectively; PDI - polydispersity index.

confirmed that the copolymers with expected chemical structures have been synthesized.

According to SEC analysis, all the obtained materials were characterized by high molecular weights (M_n, M_w) and a polydispersity index (PDI) close to 2, typical of polycondensates (Table 1). These data further confirms that the polymerization process was successful and allow to exclude an effect of the molecular weight on the properties described below.

3.2. Thermal and structural characteristics of PTF and PTFcoDod copolymers

The thermal properties of PTFcoDod copolymers were examined by DSC analysis, by heating/cooling scans at rates of 10, 5, 3 and 1 °C/min. The obtained thermograms recorded during the first heating and cooling cycles and the second heating cycle at a rate of 10 °C/min are shown in Fig. 1a and Fig. 1b, respectively, while the relative thermal data are listed in Table 2. Moreover, Fig. 1c presents glass transition temperature (T_g), melting temperatures (T_{m1}, T_{m2}) and cold crystallization

Table 2
Thermal transitions determined from 1st heating DSC scans at a heating rate of 10 °C/min and values of crystallinity degree (XRD) before and after annealing of PTF and PTFcoDod random copolymers.

Sample	DSC T_g [°C]	ΔC_p [Jg^{-1}°C^{-1}]	T_{cc} [°C]	ΔH_{cc} [Jg^{-1}]	T_{m1}, T_{m2} [°C]	ΔH_{m1}, ΔH_{m2} [Jg^{-1}]	XRD X_c [%]	X_{c_a} [%]
PTF	62	0.39	126	29	173	29	-	20
PTF5Dod	44	0.42	135	0.5	166	0.5	-	22
PTF15Dod	23	0.37	114	0.7	149	1.6	0.6	21
PTF25Dod	2	0.14	-	-	51; 125	4.9; 30	21	22
PTF35Dod	-14	0.23	-	-	55; 105	6.6; 28.4	20	22
PTF45Dod	-21	0.23	-	-	52; 94	7.7; 20.3	14	15
PTF55TDod	-28	0.11	-	-	50; 77	12.5; 19.5	15	16

T_g – glass transition temperature; ΔC_p - heat capacity; T_{cc} – cold crystallization temperature; T_m – melting temperature; ΔH_{cc}, ΔH_m – enthalpy of cold crystallization and melting, respectively; X_c - degree of crystallinity before annealing; X_{c_a} - degree of crystallinity after annealing (PTF, PTF5Dod, PTF15Dod annealed at 100 °C, 1 h; PTF25Dod, PTF35Dod, PTF45Dod annealed at 70 °C, 1 h; PTF55Dod annealed at 50 °C, 1 h).

temperature (T_{cc}) determined from first heating scan (10 °C/min) as a function of the molar fraction of TDod co-units in the copolymer. During the first heating scan at a rate of 10 °C/min, PTF, PTF5Dod and PTF15Dod showed cold crystallization and subsequent melting (Fig. 1a, Fig. 4S, dashed line).

These phenomena became less intense after copolymerization. Moreover, the homopolymer and the copolymer with the smallest amount of co-unit turned out to be amorphous ($\Delta H_{cc} = \Delta H_m$), while PTF15Dod was slightly semicrystalline ($\Delta H_{cc} < \Delta H_m$). For copolymers with a higher content of aliphatic co-units ($\geq$ 25 mol% TDod) no cold crystallization occurred, but two melting endotherms were observed, the former (T_{m1}) at almost constant temperature of 50°C, the higher melting one (T_{m2}) progressively shifted towards lower temperatures as the content of TDod units increased (Fig. 1c, Table 2). Such a phenomenon is typical for random copolymers in which both sequences are able to crystallize (Pérez-Camargo et al., 2018; Wang and Deng, 2019) and is related to the formation of smaller and less perfect crystallites. These multiple endotherms can be also due to the melting-crystallization-melting of crystals with low degree of perfection, which develop as a consequence of copolymerization (Furushima et al., 2018; Toda et al., 2016). This hypothesis will be evaluated by XRD analysis, which will be discussed in the following. If the T_g values are compared, it must be reminded that the non-linear axis of rotation and smaller angles between carbon atoms in the furan ring, compared to the benzene ring, limit the mobility of PTF chains, which results in a higher T_g of PTF, compared to PTT (Gromov et al., 2010). Conversely, PTFcoDod copolymers are characterized by long aliphatic chains and, therefore, greater molecular chain mobility than the previously investigated copolymers based on suberic and sebacic acid (Zubkiewicz et al., 2025, 2022). PTDod, like other poly (trimethylene alkanedicarboxylate)s has a glass transition temperature below room temperature (Bikiaris et al., 2008) and meting point of 67 °C (Zhou et al., 2019). Consequently, with the increase in the content of aliphatic dicarboxylic acid units, T_g decreased from 62 °C for PTF to −28 °C for PTF55Dod (Fig. 1c). Of note, the physical aging phenomena, in correspondence of T_g jump, can be observed in the homopolymer and PTF5Dod sample.

Calorimetric profiles obtained during slower heating and cooling rates are presented in SI (Fig. 3S). As a general trend, all the samples, except for PTF55Dod, showed cold crystallization and subsequent melting. As expected, the crystallization temperature progressively shifted towards lower temperatures as the heating rate decreased. Lastly, physical aging progressively disappeared by decreasing the heating rate.

During the second heating (at a standard heating rate of 10 °C/min), neither cold crystallization nor melting of the copolymers was recorded (Fig. 1a). However, these effects were visible, for all synthesized materials, at slower heating rates (Fig. 3S). This is reasonable, considering that FDCA-based polyesters are characterized by much slower crystallization compared to TA-based ones (Terzopoulou et al., 2020). As reported in the literature, this is probably related to the nonlinear nature of FDCA and to the presence of a permanent dipole, which hinders crystallization by inhibiting the furan ring motions (Burgess et al., 2014; Knoop et al., 2013; Wang et al., 2017a). Regardless of the cooling rate, no crystallization was observed in the thermograms (Fig. 1a, Fig. 3S).

X-ray studies (Fig. 3S) showed that PTF and copolymers with up to 15 mol% of TDod co-units were amorphous, while the copolymers richer in TDod units developed a crystalline structure typical of PTF (Zubkiewicz et al., 2022), with values of degree of crystallinity (X_c) ranging between 20 % and 25 % (Fig. 1d). These values are in agreement with XRD results (Table 2, Fig. 4S).

Furthermore, the impact of annealing treatment on the crystallinity of the samples was examined (Fig. 3S). As expected, the amorphous samples developed a crystalline phase, with values of X_c reaching 20 %, while for the already semicrystalline samples, a slight increase in X_c

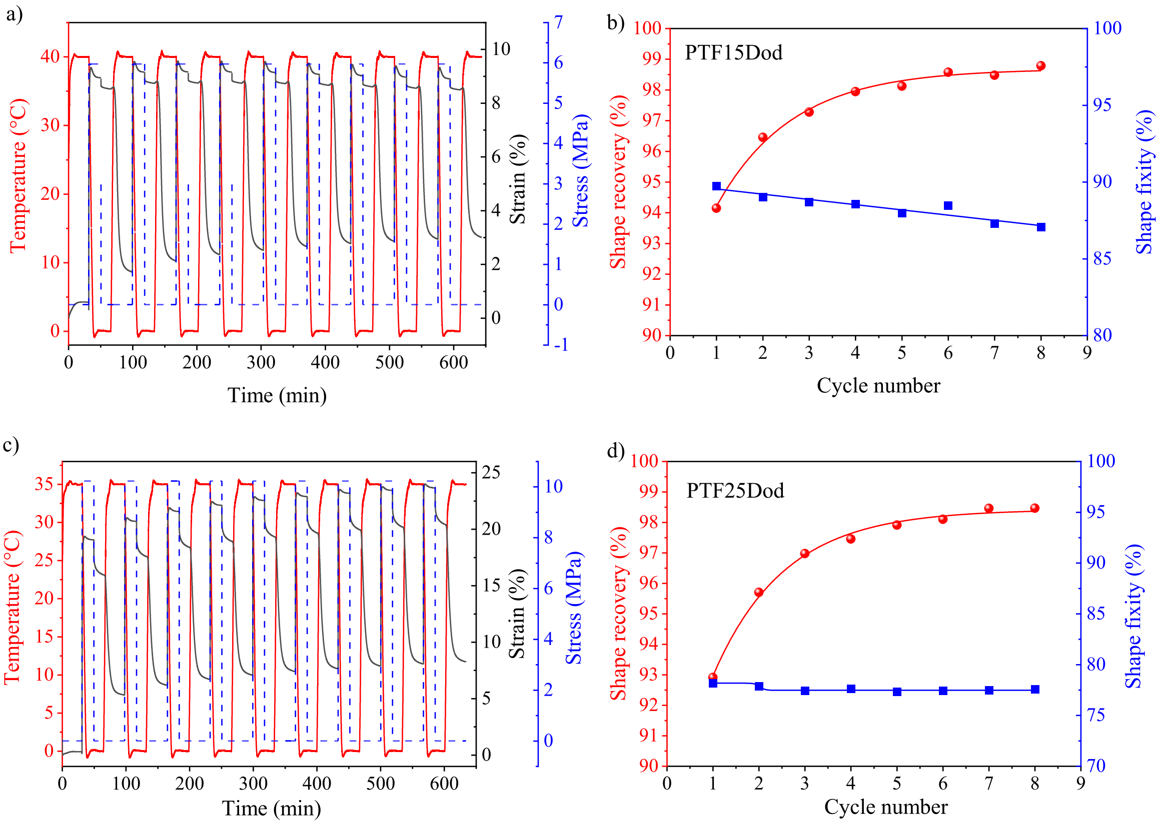

Fig. 3. Multiple thermomechanical cycles for (a) PTF15Dod and (c) PTF25Dod copolymers and their shape fixity (R_f) along with shape recovery efficiency (R_r) vs cycle number (b, d).

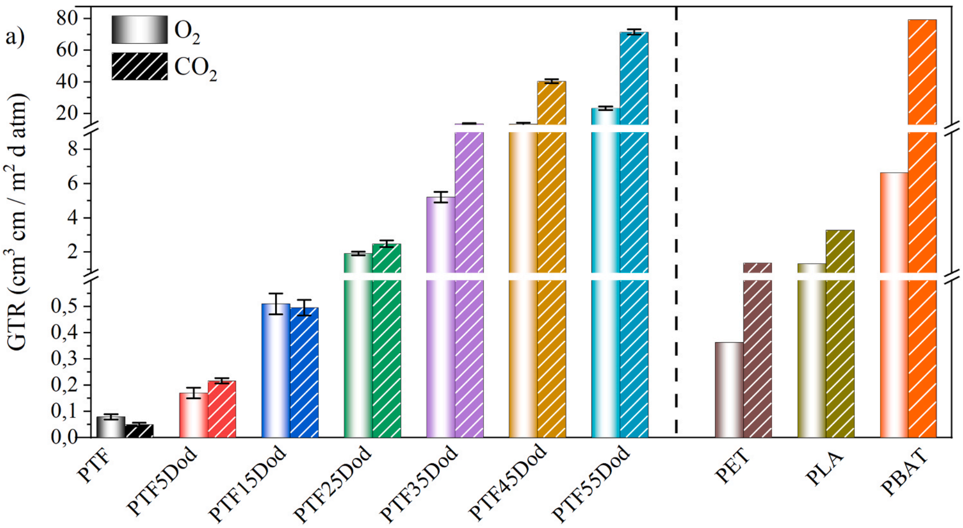

Fig. 4. Gas transmission rate of oxygen (O_2) and carbon dioxide (CO_2) for PTF, PTFcoDod copolymers and some commercially available polyesters (PET (Genovese et al., 2017), PLA (Siracusa et al., 2012), PBAT (Huang et al., 2020).

values was observed. As to the position of the peaks, this was not altered, except for the central peak, at around $2\theta = 22$ °, in line with what already observed for other copolymers of PTF containing long aliphatic co-units (Zubkiewicz et al., 2022).

Thermogravimetric analysis proved the high thermal stability in both inert and oxidizing atmospheres, slightly increasing with the amount co-unit. PTFcoDod copolymers were thermally stable up to at least 350 °C and thereafter they exhibited two-step thermal degradation in both argon and air atmospheres (Fig. 5S, Table 2S).

3.3. Physicochemical and mechanical properties of PTF and PTFcoDod copolymers

The results of the water contact angle (WCA) values are presented in Fig. 2. PTFcoDod copolymers are all more hydrophobic than PTF, due to the presence of a long-chain diacid co-unit. As the TDod content increases up to 45 mol%, a progressive increase in hydrophobicity is observed, which is manifested by a rise in WCA values from 86° to 105°. Then, for PTF55Dod copolymer, a slight decrease in the wettability is observed, which is presumably related to the phase inversion (predominance of the TDod phase) and the disruption of the structural uniformity (Song et al., 2024).

Table 3 shows the results of mechanical properties tests in static tension for non-annealed and annealed samples. Representative stress-strain curves are presented in the SI (Fig. 6S). PTF and PTF5Dod copolymer were characterized by high stiffness and brittleness, which manifests in high Young's modulus values, and low elongation at break, that did not exceed 3 %. This is reasonable, as at room temperature they are both glassy ($T_g > T_{room}$). The results obtained for neat PTF are in good agreement with previously reported literature data (Terzopoulou et al., 2020). The slightly higher modulus of PTF5Dod compared to neat PTF can be attributed to its higher molecular weight, which reduces chain mobility, counteracting the effect of the lower T_g. In contrast to PTF, the PTDod has low tensile modulus of 132 MPa with tensile strength of 28 MPa and high elongation at break of 1550 % (Zhou et al., 2019).

With the increase in the TDod co-units' content, the nature of the stress-strain curves changed significantly and a notable decrease in stress at break and Young's modulus was visible (Table 3). PTF15Dod copolymer was characterized by the highest elongation at break, that was over 100 times greater than PTF. According to the XRD and DSC results (Table 2, Fig. 1d), PTF15Dod copolymer is amorphous, with a T_g around room temperature, characteristics that ensure high chain flexibility, as already observed for the same copolymeric composition containing shorter aliphatic co-unit (Zubkiewicz et al., 2025, 2022). Conversely, for the copolymers with a higher content of TDod co-units ($\geq$ 25 mol%), a progressive decrease in all the mechanical parameters can be observed. This mechanical behavior results from two counteracting effects: on one side all the samples become semicrystalline, while T_g progressively decreases by increasing TDod amount. Accordingly, the decrease in Young's modulus and in the stress at break must be ascribed to the progressively increasing amount of co-unit, which results in higher chain flexibility (lower T_g). Conversely the lower and almost comparable values of the elongation at break result from the presence of a not negligible amount of crystalline phase.

After annealing, all the samples were characterized by quite similar values of mechanical parameters compared to those before annealing (Table 2). The only exception was PTF15Dod, which underwent significant changes: the development of a consistent amount of crystallinity (Fig. 1d) resulted in an almost 5-fold increase in the Young's modulus, a 3-fold increase in stress at break and a more than 7-fold decrease in the elongation at break.

3.4. Shape memory properties of PTF and PTFcoDod copolymers

Based on the performed DSC analysis, PTFcoDod random copolymers containing 15 and 25 mol% of TDod units may exhibit a thermally induced shape memory effect. Thus, in order to assess the stability of the temporary shape (shape fixity (R_f)) and the return to the original shape (shape recovery (R_r)), eight shape memory cycles for PTF15Dod and PTF25Dod copolymers were measured. The thermomechanical cycles of PTF15Dod and PTF25Dod copolymers are shown in Fig. 3. PTF15Dod copolymer was deformed at a temperature of 40 °C, above its T_g. Over 8 experimental cycles, the stability of the temporary shape decreased by more than 2 %. After obtaining a temporary shape and reheating, PTF15Dod copolymer returned to its original shape in more than 94 %, achieving the highest R_r value of 98.8 % in the last cycle tested. Low R_r values in the first cycles are probably related to the sample processing history (Paszkiewicz et al., 2021; Shi and Weiss, 2014; Xie et al., 2016). It can be concluded that carrying out preliminary processing through the so-called training, i.e. the initial implementation of several thermomechanical loading cycles, will result in high shape recovery parameters. PTF25Dod copolymer was heated to a temperature of 33 °C. Although compared to PTF15Dod copolymer PTF25Dod samples exhibited lower R_f values, they were stable regardless of the cycle number. Similarly to PTF15Dod copolymer, the obtained R_r values for

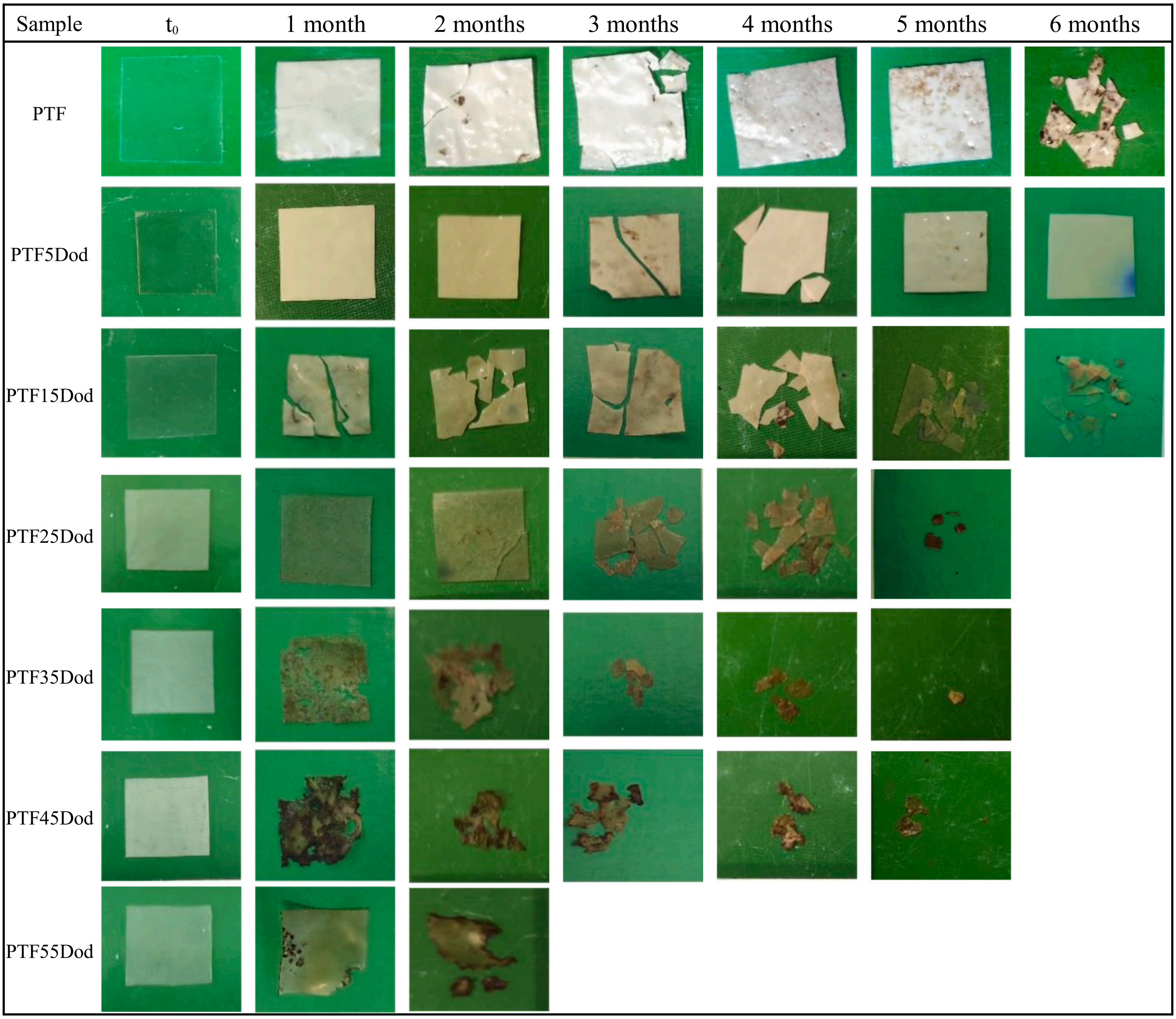

Fig. 5. Pictures of PTF and PTFcoDod samples before and after the composting process at different timepoints.

PTF25Dod increased with subsequent cycles up to 98.5 %. Based on the conducted studies, one can state that investigated random copolymers can be considered as promising SMPs, in particular due to their high ability to return to their original shape.

3.5. Gas permeation properties of PTF and PTFcoDod copolymers

PTFcoDod random copolymers were tested for their barrier performances to oxygen (O_2) and carbon dioxide (CO_2). The obtained values of gas transmission rates (GTR) are presented in Fig. 4 and listed in Table 3S. Among the tested materials, the lowest GTR values were obtained for PTF and PTF5Dod copolymer, this last being characterized by over 2 times lower O_2 permeability and over 6 times lower CO_2 permeability than PET, and almost 8 times lower O_2 permeability and over 15 times lower CO_2 permeability than PLA. These superior barrier properties can be ascribed to intermolecular interactions between hydrogen atoms in the furan ring and oxygen atoms in the carboxyl groups (Mao et al., 2016; Papamokos et al., 2019). Additionally, π-π stacking interactions that may arise between furan rings may be of great importance (Araujo et al., 2018; Papamokos et al., 2019). The remarkably lower permeability of PTF and PTF5Dod compared to PET may also be influenced by the significantly lower values of their free volume (Irska et al., 2021; Singh et al., 2015; Wang et al., 2019; Zubkiewicz et al., 2022). As the content of TDod units in the copolymers increased, the barrier properties significantly deteriorated, due to the decrease of high performant furan moieties per chain unit, as well as to the development of a crystalline phase. As already observed for other furan-based polyesters, the interchain interactions responsible for the noteworthy high gas barrier properties of this class of materials are maximized when the crystalline phase is absent (Guidotti et al., 2020; Quattrosoldi et al., 2022). Moreover, the presence of crystals results in the formation of interphases between crystalline and amorphous phase, resulting in higher permeability. However, even though PTF45Dod and PTF55Dod copolymers are characterized by the worst barrier properties among the obtained materials, they are still comparable to the commercially available PBAT copolymer (Ecoflex) used as a biodegradable and flexible packaging material (Huang et al., 2020).

PTFcoDod copolymers are also characterized by higher GTR values than copolymers containing 6 and 8 methylene groups in the aliphatic chain of dicarboxylic acid, with the same composition (Zubkiewicz et al., 2025, 2022).

As can be seen in Fig. 4, the perm-selectivity ratio (ratio between

Table 3
Water contact angle and tensile properties of PTF and PTFcoDod copolymers.

Sample	Water contact angle	Young's modulus	Stress at break	Strain at break
	(°)	(MPa)	(MPa)	(%)
PTF	86 ± 4	2460 ± 76	79 ± 3	3 ± 0.2
PTF, 100 °C, 1 h		2707 ± 164	73 ± 1	3 ± 0.4
PTF5Dod	88 ± 4	3241 ± 168	47 ± 5	2 ± 0.3
PTF5Dod, 100 °C, 1 h		3234 ± 404	51 ± 2	2 ± 0.3
PTF15Dod	93 ± 4	430 ± 79	11 ± 0.3	309 ± 28
PTF15Dod, 100 °C, 1 h		2060 ± 163	34 ± 1	41 ± 7
PTF25Dod	98 ± 2	360 ± 14	14 ± 0.3	49 ± 3
PTF25Dod, 70 °C, 1 h		378 ± 17	16 ± 0.2	56 ± 10
PTF35Dod	105 ± 4	188 ± 11	10 ± 0.1	31 ± 12
PTF35Dod, 70 °C, 1 h		190 ± 14	12 ± 0.2	38 ± 4
PTF45Dod	105 ± 3	105 ± 4	7 ± 0.2	50 ± 18
PTF45Dod, 70 °C, 1 h		106 ± 5	8 ± 0.1	66 ± 10
PTF55Dod	99 ± 2	67 ± 1	5 ± 0.1	49 ± 10
PTF55Dod, 50 °C, 1 h		81 ± 2	6 ± 0.3	63 ± 16
PTDod*	-	132 ± 17	28 ± 3.7	1550 ± 35

* Tensile data for PTDod with $M_n = 32\,800$ g mol^{-1} and PDI = 1.74, determined at rate of 10 mm min^{-1} (Zhou et al., 2019).

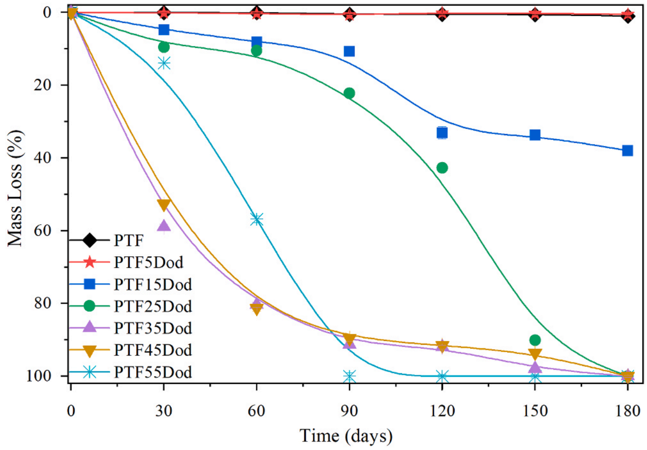

Fig. 6. Percentage mass loss of PTF and PTFcoDod copolymers as a function of incubation time in compost.

CO_2-TR and O_2-TR) was greater than 1 in all cases, except for PTF15PTDod, in which this parameter was slightly lower than 1. Even though O_2 molecules are smaller than CO_2, the CO_2 diffuses faster, thanks to its high solubility coefficient (Robertson, 2012). A similar relationship was observed also in previous works (Guidotti et al., 2020; Zubkiewicz et al., 2025).

3.6. Biodegradation of PTFcoDod copolymers

Biodegradation was assessed by placing samples of PTF and PTFcoDod copolymers in compost for a period from 1 to 6 months. Distinct change in the appearance of the samples was visible just after 1 month of incubation (Fig. 5). As shown by DSC data (Table 2), the incubation temperature, of 58 °C, was close to the T_g of PTF and higher than the T_g of all the copolymers. Thus, amorphous copolymers underwent crystallization and became opaque and more brittle. As it is known, PTF is classified as non-biodegradable polyester (Poulopoulou et al., 2020). It is therefore not surprising that 6 months turned out to be insufficient to degrade the homopolymer. Nevertheless, significant fragmentation was observed (Fig. 4). As can be seen in Fig. 4, most of the copolymers were almost completely degraded after 5 months of composting, due to the presence of aliphatic dicarboxylic acid units, which contributed to a significant acceleration of PTF degradation. For example. in the case of PTF55Dod copolymer, 3 months of incubation were enough to thoroughly degrade the sample. The above observations were confirmed by measuring the gravimetric mass loss of the polymeric films after specific incubation time points in compost (Fig. 6). As it can be seen, PTF and PTF5Dod showed negligible weight loss even after 6 months of incubation. Conversely, the degradation speeded up in the other copolymers, proportional to the amount of aliphatic co-unit. For copolymers containing 5 and 15 mol% TDod units, 6 months was insufficient time to degrade, while in all the other cases, the weight loss was complete. Moreover, PTF45Dod and PTF55Dod copolymers were degraded by over 50 % after just one month of incubation. Compared to previous results obtained on copolymers containing shorter aliphatic chains in dicarboxylic acid co-units (i.e. suberic acid and sebacic acid) (Zubkiewicz et al., 2025, 2022), it can be seen that longer TDod units did not significantly change the degradation rate.

However, PTF15Dod degraded much faster than the copolymers containing the same molar amount of suberic and sebacic co-units, whose mass loss after 4 months of incubation did not exceed 10 %, as a result of its T_g, very close to room temperature and lower than those of its homologues containing shorter diacid co-units. Conversely, the PTF25Dod copolymer was characterized by smaller mass losses than PTF25TSeb and comparable to PTF25TSub copolymer. It is possible that the crystalline phase developed by the TSeb-containing copolymer was less perfect (lower T_m) and easier to be attacked by the microorganisms inside the compost.

The thermal characteristics of partially degraded samples and their relative blanks (incubated at 58 °C without compost) were also examined, and the obtained data are presented in Fig. 7S and Table 4S. The calorimetric curves of all the blanks show multiple endothermic phenomena, indicating the appearance of annealing peaks for amorphous samples and the shift towards higher temperatures of the endothermic phenomena in the already semicrystalline materials, due to the permanence at 58 °C. As to the partially degraded samples, a similar trend was observed, the only difference being a slight increase in the melting enthalpies, due to the enzymatic attack. Moreover, with the incubation time, melting enthalpies increased and melting temperatures shifted towards higher values, which resulted from the formation of a more perfect crystalline phase.

Last, ^{1}H NMR measurements were performed on partially degraded PTF5Dod, PTF15Dod and PTF25Dod samples after 4 months of incubation, to check if any variation in chemical composition occurred due to the permanence in compost. According to the intensities of the integrated signals obtained from these spectra (Fig. 8S), the actual composition did not change upon composting, suggesting that both the co-units undergo degradation at the same rate. Moreover, if the region around 3.65 ppm is observed (Fig. 9S), some remarkable differences in the spectra before and after composting studies are evident. Indeed, differently from non-composed samples, after 4 months of incubation the signals of the methylene protons in α position to the terminal hydroxyl groups became evident in all cases, indicating that some molecular weight loss occurred.

4. Conclusions

This work was devoted to the study of novel, environmentally friendly PTFcoDod random copolymers with different content of aliphatic dicarboxylic acid units. The PTFcoDod copolymers were synthesized by means of a two-step melt polycondensation process. According to the thermal characterization, the high thermal stability, peculiar property of PTF, was preserved also in the copolymers, while the main thermal transitions were tuned according to the chemical composition. On the basis of gas permeation results, one can conclude that TDod units contribute to the deterioration of the barrier properties of PTF, but all the tested materials are still characterized by better or comparable gas transmission rate values than PET, PLA or PBAT. For instance, PTF15Dod copolymer was characterized by an elongation at break of over 300 % and better barrier properties than PLA. Moreover, it was found that copolymers containing 15 and 25 mol% of aliphatic dicarboxylic acid comonomers show a highly repeatable, thermally induced shape memory effect. The obtained random copolymers with a sufficient amount of co-unit also undergo biodegradation in compost. Indeed, as the share of TDod units increased, the degradation process was accelerated and copolymers containing 25 mol% of TDod units degraded completely after a few months. Considering all functional properties, by copolymerization of PTF with long TDod units, it was possible to obtain materials with good barrier properties, giving them improved flexibility, which will increase the application possibilities, especially in the packaging industry.

CRediT authorship contribution statement

Agata Zubkiewicz: Writing – original draft, Investigation. **Giulia Guidotti:** Writing – review & editing, Investigation. **Anna Szymczyk:** Writing – review & editing, Writing – original draft, Validation, Supervision, Conceptualization. **Valentina Siracusa:** Writing – review & editing, Investigation. **Nadia Lotti:** Writing – review & editing, Validation, Funding acquisition. **Rafael Sablong:** Investigation. **Michelina Soccio:** Writing – review & editing, Validation.

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.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.indcrop.2025.122378.

Data availability

Data will be made available on request.
PTFcoTDod copolymers (Mendeley Data)

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