

Partially bio-based and tough polyesters, poly(ethylene 2,5-thiophenedicarboxylate-co-1,4-cyclohexanedimethylene 2,5-thiophenedicarboxylate)s

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Abstract. Novel tough bio-based polyesters poly(ethylene 2,5-thiophenedicarboxylate-co-1,4-cyclohexanedimethylene 2,5-thiophenedicarboxylate)s (PECTFs) were synthesized from 2,5-thiophenedicarboxylic acid (TDCA), 1,4-cyclohexanedimethanol (CHDM) and ethylene glycol (EG). The microstructure, thermal and mechanical properties were investigated. Poly(ethylene 2,5-thiophenedicarboxylate) (PETF) displayed the glass transition temperature (~64 °C) and tensile strength (~72 MPa) similar to poly(ethylene terephthalate) (PET). However, the nonlinear structure of TDCA resulted in an angle of 148° between carboxylic acid carbons and the S atom resulted in a permanent dipole, so the thiophene ring-flipping was hindered and the low elongation at break (~24%) was observed for PETF. The peak corresponding to the secondary relaxation shifted to lower temperature due to the incorporation of CHDM, which yielded ductile copolyesters with high elongation at break. When the CHDM content was equal to or higher than 29%, a high elongation at break (>160%) was observed.

Keywords: material testing, mechanical properties, thermal properties

1. Introduction

Due to environmental problems and the depletion of oil resources, bio-based materials have attracted more and more people's attention and become a research hot spot [1–5]. Previously, the industrialized bio-based polyesters mainly include polylactic acid (PLA), polyhydroxyalkanoates (PHA), polyhydroxybutyrate (PHB), and poly(butylene succinate) (PBS).

Recently, poly(ethylene furanoate) (PEF) derived from 2,5-furandicarboxylic acid (FDCA) becomes the focus of research and development due to the excellent barrier properties and high chemical resistance [6–8]. Hence, PEF is suitable for the preparation of films and 3D printing materials. A reduction in oxygen permeability of ~11× and carbon dioxide permeability of 19× at 1 atm was observed at 35 °C

for PEF compared to poly(ethylene terephthalate) (PET) [9, 10]. Glass transition temperature of PEF is higher than that of poly(ethylene terephthalate) (PET). However, the melting temperature and crystallization rate are low [11]. The comparison of the hydrolysis of PEF and PET by two cutinases is also researched by Weinberger *et al.* [12]. Results suggested PEF films were enzymatically hydrolyzed 1.7 times faster than PET films. Compared with the fully amorphous films, PET films with two different crystallinities (10 and 20%) strongly decreased the enzymatic hydrolyzability. However, the decreasing trend was much more gradual for PEF films.

2,5-Thiophenedicarboxylic acid (TDCA) is another bio-based diacid and can be synthesized by the reaction of adipic acid and thionyl chloride [13].

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Meanwhile, adipic acid can be produced from glucaric or muconic acid [14]. The synthetic routes of 2,5-thiophenedicarboxylic acid (TDCA) from petrochemicals and biomass are summarized in Figure 1 [15]. The structure of TDCA is similar to that of FDCA. The oxygen atom in the furan ring is replaced by the sulfur atom. The angle between carboxylic acid carbons (148°) in the thiophene ring is larger than that (129.4°) in the furan ring. Meanwhile, the resonance energy of the thiophene ring is higher than that of the furan ring and the dipole moment of the thiophene ring is lower than that of the furan ring. As reported from Lotti, poly(propylene 2,5-thiophenedicarboxylate) (PPTF) is indeed more thermally stable than poly(propylene 2,5-furandicarboxylate) (PPF) due to the higher resonance energy of the thiophene ring. Meanwhile, compared with PPF, T_g of PPTF is lower and the crystallizing ability of PPTF is higher due to the larger angle between carboxylic acid carbons (148°) in the thiophene ring. The permeability behavior of PPTF became better than that of PPF with increasing the relative humidity due to a lower plasticizer effect of water because of the weak polar nature of the thiophene ring. Some TDCA-based polyesters have been synthesized, such as poly(propylene 2,5-thiophenedicarboxylate) (PPTF) [16], poly(butylene 2,5-thiophenedicarboxylate) (PBTF) [17], and poly(butylene adipate/2,5-thiophenedicarboxylate)s (P(BAxBTFy)) [18]. At 23°C , PPTF shows excellent moisture resistance compared to poly(propylene 2,5-furandicarboxylate) (PPF). In addition, a reduction in oxygen permeability of $2.0\times$ and carbon dioxide permeability of $4.75\times$ was observed at 23°C for PBTF compared to PEF.

Ethylene glycol (EG) can be synthesized from bio-ethanol. 1,4-Cyclohexanedimethanol (CHDM) is a diol with six-member ring. Recently, the use of CHDM as a comonomer of 1,4-butanediol (BDO) is a well-known approach to increase the glass transition temperature of poly(butylene 2,5-furandicarboxylate) (PBF). In addition, CHDM was employed to enhance the toughness and crystallization ability of PEF. However, when the molar percent of CHDM unit was high (59%), the copolyester showed the highest elongation at break (186.3%).

Poly(ethylene 2,5-thiophenedicarboxylate) (PETF) has been synthesized by other researchers. However, the tensile properties are not characterized. In this paper, the tensile properties are characterized for PETF for the first time. However, PETF with high tensile strength exhibits the low elongation at break. In order to solve the problem, poly(ethylene 2,5-thiophenedicarboxylate-co-1,4-cyclohexanedimethylene 2,5-thiophenedicarboxylate)s (PECTFs) and poly(1,4-cyclohexanedimethylene 2,5-thiophenedicarboxylate) (PCTF) were synthesized by incorporating 1,4-cyclohexanedimethanol (CHDM). The effects of CHDM on sequence structure, crystallization behaviors, thermal properties, and mechanical properties were investigated.

1. Experimental section

2.1. Materials

2,5-Thiophenedicarboxylic acid (TDCA, 99%) was purchased from Heowns Biochem Technologies Limited Liability Company (China). 1,4-Cyclohexanedimethanol (CHDM) (99%) with 67 mol%

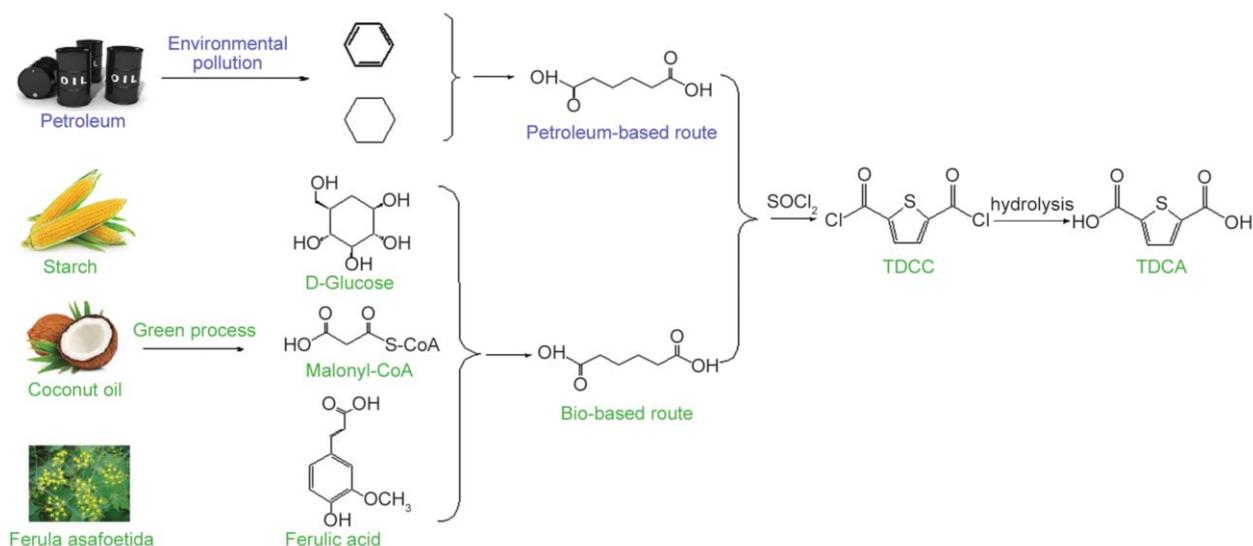


Figure 1. The synthetic routes of 2,5-thiophenedicarboxylic acid (TDCA) from petrochemicals and biomass.

trans-isomer was purchased from Aladdin Reagent Co. Ltd (Shanghai, China). Ethylene glycol (EG, 99%) were purchased from Sinopharm Chemical Reagent limited corporation (China). Tetrabutyltitanate (TBT, 99%) were purchased from Tianjin Guangfu Fine Chemical Research (China).

2.2. Synthesis of PETF, PCTF and PECTFs

Poly(ethylene 2,5-thiophenedicarboxylate) (PETF), poly(1,4-cyclohexanedimethylene 2,5-thiophenedicarboxylate) (PCTF) and poly(ethylene-co-1,4-cyclohexanedimethylene 2,5-thiophenedicarboxylate)s (PECTFs) were synthesised, using a standard two steps polycondensation process. TBT (30 μ l/0.1 mol TDCA), TDCA (0.2 mol), and diols (EG and/or CHDM) (diol/TDCA = 1.6 molar ratio) were introduced into the reactor with N₂ inlet. The reactor was heated to 230 °C and stirred for 2 h. A vacuum (50 Pa) was applied gradually to the polycondensation system after 0.5 h. The reactor was heated to 250 °C The reaction was stopped when the rod-climbing phenomenon occurred. Finally, the reaction pressure was returned to the normal atmospheric pressure by the introduction of N₂ and the product was cooled to room temperature by air naturally. All samples were brown and transparent. Finally, the samples were dried under vacuum at 60 °C for 24 h and sealed. PECTF29, PECTF49, PECTF77 denoted 29, 49 and 77 mol% 1,4-cyclohexanedimethylene 2,5-thiophenedicarboxylate unit (CT) in the copolyesters determined by ¹H NMR.

2.3. Analysis

Weight-average molecular weight (M_w) and molecular weight distribution (D) were determined by GPC using a Waters 1515 HPLC apparatus (USA). Hexafluoroisopropanol (HFIP) containing 5 mmol/l sodium trifluoroacetate (CF₃COONa) was used as the solvent at 30 °C and the solvent flow rate was 1.0 ml/min. M_w and D were determined using polymethyl methacrylate (PMMA) standards with a narrow D .

¹H NMR spectra were recorded with a Bruker spectrometer (Germany, 600 MHz) in CF₃COOD. Tetramethylsilane (TMS) was used as the internal standard. ¹³C NMR spectra were recorded using the same NMR spectrometer (150 MHz). The molar percentage of 1,4-cyclohexanedimethylene 2,5-thiophenedicarboxylate (CT) unit in copolymers (Φ_{CT}), number-average sequence length of CT unit ($L_{n,CT}$),

number-average sequence length of ethylene 2,5-thiophenedicarboxylate (ET) unit ($L_{n,ET}$) and the degree of randomness (R) were calculated.

The thermal transitions and non-isothermal crystallization behavior were recorded by differential scanning calorimeter (DSC) (Switzerland Mettler Toledo DSC 1 differential scanning calorimeter, Mettler-Toledo International Inc., Zurich, Switzerland). The samples were placed in alumina crucibles. Nitrogen gas flow rate was 50 ml/min. First, PETF, PCTF and PECTFs were cooled to –30 °C and then heated to 290 °C at a rate of 10 °C/min, the temperature was hold for 3 min, and cooled again to –30 °C at a rate of 10 °C/min. Finally, PETF, PCTF and PECTFs were heated again to 290 °C at a rate of 10 °C/min. Melting temperature (T_m), melting enthalpy (ΔH_m), cold crystallization temperature (T_{cc}) and its enthalpy (ΔH_{cc}) were obtained on the 1st heating scan at 10 °C/min. The glass transition temperature (T_g) was taken as the midpoint of the step transition observed on the 2nd heating scan at 10 °C/min.

Thermogravimetric analysis (TGA) was performed on a Mettler TGA/DSC 1 instrument. The samples (5 mg) were placed in ceramic crucibles. Nitrogen gas flow rate was 50 ml/min. The samples were heated from 30 to 600 °C at a rate of 10 °C/min. The degradation temperature at 5% weight loss ($T_{d,5\%}$) and the residue weight at 600 °C (W_{600}) were obtained.

The tensile properties of PETF, PCTF and PECTFs were measured with Instron-1121 tester according to ASTM D638. The crosshead speed was 5 mm/min. The specimens were prepared by injection molding. The dimension of middle segment was 3.20 mm thickness \times 3.18 mm width. Five samples were tested. Dynamic thermomechanical analysis (DMA) of PETF, PCTF and PECTFs was carried out using a Dynamical Mechanical thermal Analyzer DMA+450 (Metravib) in tensile mode. The samples (50 mm length \times 5 mm width \times 1.5 mm thickness) were prepared by injection molding method. A dynamic displacement of 20 μ m was applied at frequencies of 10 Hz. The specimens were run from –130 to 40 °C in at a rate of 2 °C/min.

3. Results and discussion

3.1. Synthesis and structures

PETF, PCTF, and PECTFs were synthesized from EG, CHDM and TDCA. Figure 2 shows GPC traces of PETF, PCTF and PECTFs. The weight-average molecular weights (M_w) of all polyesters prepared

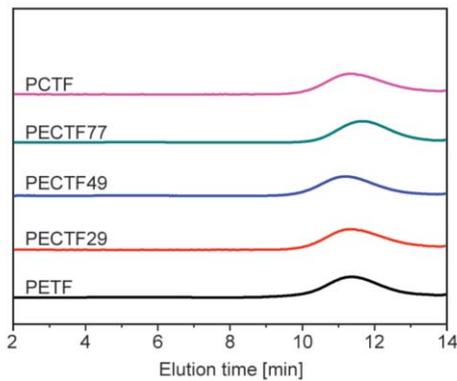


Figure 2. GPC traces of PETF, PCTF and PECTFs.

were higher than $10000 \text{ g}\cdot\text{mol}^{-1}$, and the molecular weight distribution (D) was 1.9–3.3 (Table 1). We don't find a shoulder at higher molecular weight from GPC chromatograms. PETF, PCTF, and PECTFs were synthesized by bulk polymerization method.

The viscosity of the system was high at the reaction temperature, which made it difficult to react evenly. Hence, high D values were observed. PET and PEF also exhibit similar high D (2.58 and 2.63) [19]. Because CHDM is more rigid than EG, the viscosity of PCTF is higher than that of PETF. Meanwhile, the boiling point of CHDM is higher than that of EG, so CHDM is difficult to remove during the polymerization and the polymerization rate is slower. Based on the above two reasons, the molecular weight of PCTF is the lowest. Figure 3 shows the synthetic route of PECTFs. Figure 4 shows chemical structures of ETE, ETC, and CTC unites in PECTFs. Figure 5 shows ^1H NMR spectra of PETF, PCTF, and PECTFs. For PETF, the peaks at 4.63 ppm (**a**) and 7.72 ppm (**b**) were assigned to the CH_2 in EG unit and CH in the thiophene ring, respectively. For PCTF,

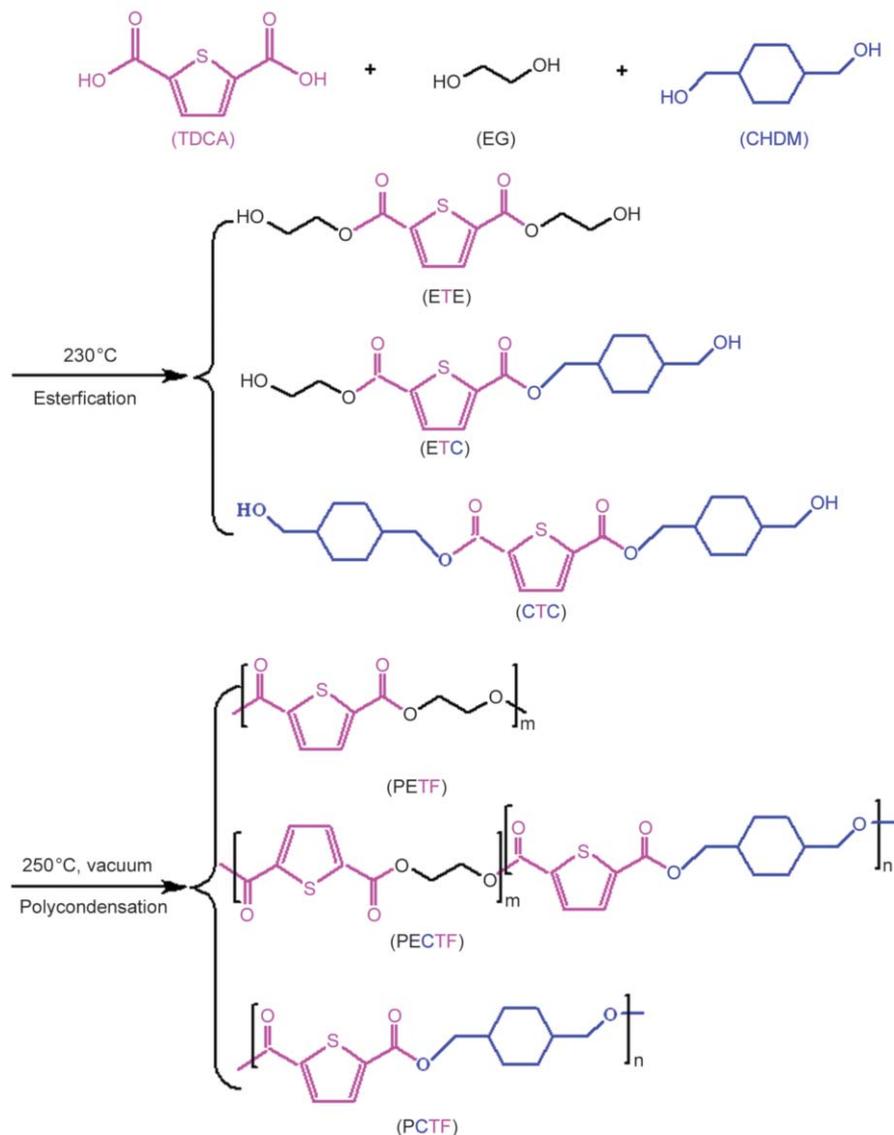
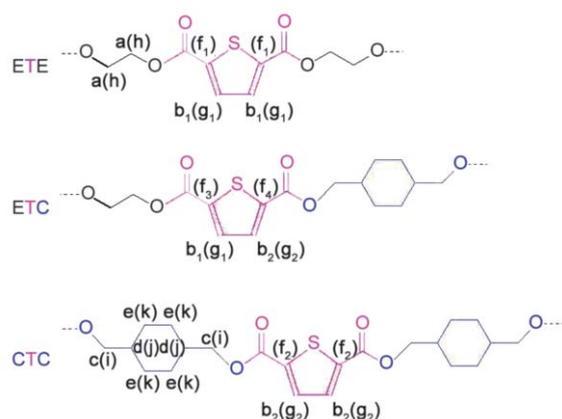


Figure 3. The synthetic route of PETF, PCTF and PECTFs.

Table 1. Microstructures and molecular weights of PETF, PCTF, and PECTFs.

Sample	Φ_{CT} [mol%]		Φ_{trans} [mol%]		$L_{n,CT}$	$L_{n,ET}$	R	M_w [g/mol]	D	Yield [%]
	in feed	in copolymers	in feed	in copolymers						
PETF	0	0	–	–	–	–	–	36 700	3.3	85
PECTF29	20.0	29.0	33:67	30:70	1.52	3.25	0.97	32 300	1.9	86
PECTF49	37.5	49.0	33:67	31:69	1.98	2.05	0.99	40 700	3.2	88
PECTF77	60.0	77.0	33:67	32:68	4.68	1.35	0.95	20 500	2.7	88
PCTF	100.0	100.0	33:67	35:65	–	–	–	11 000	2.3	89

**Figure 4.** Chemical structures of ETE, ETC, and CTC units in PECTFs.

the peak at 7.69 ppm (c_2) was assigned to the CH in the thiophene ring. The peaks at 4.25 (d_{cis}) and 4.12 ppm (d_{trans}) were assigned to cis- and trans-methylene protons of oxymethylene in CHDM unit. The peaks at 1.96 (d_{cis}) and 1.69 ppm (d_{trans}) were assigned to cis- and trans-methylene protons of the cyclohexane ring in CHDM unit. The peaks (e_{cis}) at 1.58 and 1.46 ppm were assigned to cis-methane protons of the cyclohexane ring in CHDM unit. The peaks (e_{trans}) at 1.83 and 1.05 ppm were assigned to

trans-methane protons of the cyclohexane ring in CHDM unit.

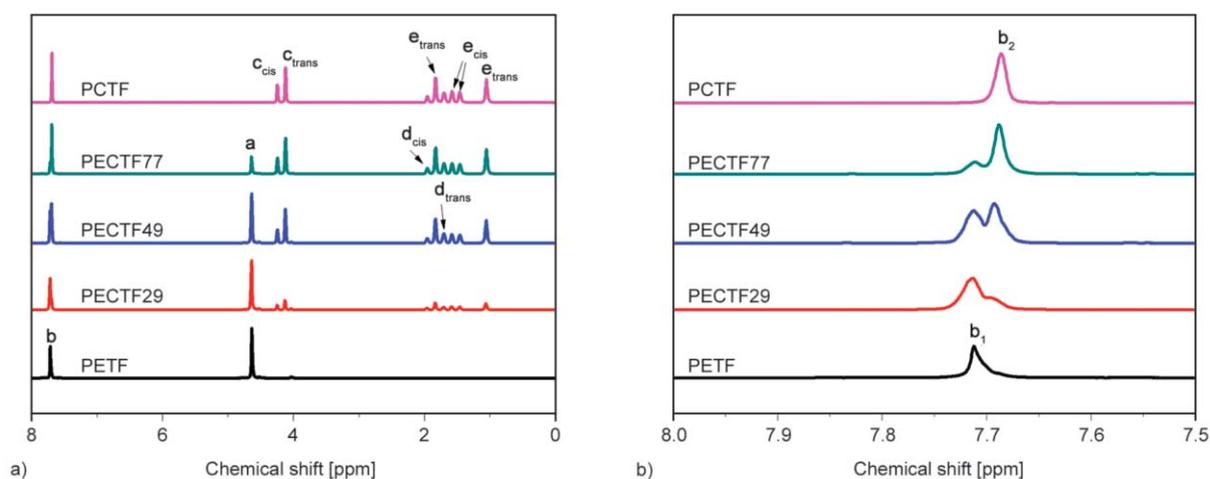
To determine the sequence distribution, PETF, PCTF, and PECTFs were characterized by quantitative ^{13}C NMR spectra. For PETF, the peak (f_1) at 130.4 ppm was assigned to the nonprotonated aromatic carbon atoms. For PCTF, the peak (f_2) at 130.8 ppm was assigned to the nonprotonated aromatic carbon atoms. However, for PECTFs, the resonance of the nonprotonated aromatic carbon atoms (f) has split into four peaks (f_1 , f_2 , f_3 , and f_4) correspond to four types of carbon atoms (Figure 4 and Figure 6). Φ_{CT} , $L_{n,CT}$, $L_{n,ET}$, R and Φ_{trans} are estimated according to Equation (1)–(5), respectively:

$$\Phi_{CT}[\text{mol}\%] = \frac{I_c}{I_a + I_c} \cdot 100 \quad (1)$$

$$L_{n,CT} = 1 + \frac{2I_{f_2}}{I_{f_3} + I_{f_4}} \quad (2)$$

$$L_{n,ET} = 1 + \frac{2I_{f_1}}{I_{f_3} + I_{f_4}} \quad (3)$$

$$R = \frac{1}{L_{n,CT}} + \frac{1}{L_{n,ET}} \quad (4)$$

**Figure 5.** 1H NMR spectra of PETF, PCTF, and PECTFs, a) the whole spectra, b) magnification of chemical shift **b**.

$$\Phi_{\text{trans}} [\text{mol}\%] = \frac{I_{\text{c,trans}}}{I_{\text{c,cis}} + I_{\text{c,trans}}} \cdot 100 \quad (5)$$

where Φ_{CT} represents the molar percentage of CT in the copolyesters. I_a and I_c represent the integrals of the corresponding peaks **a** and **c**, respectively. $L_{\text{n,CT}}$ and $L_{\text{n,ET}}$ represent the number-average sequence length of CT and ET units, respectively. R represents the degree of randomness. Φ_{trans} represents the molar ratio of trans-isomer in copolyesters.

With increasing the CHDM content, the number-average sequence length of CT unit ($L_{\text{n,CT}}$) gradually increased and the number-average sequence length of ET unit ($L_{\text{n,ET}}$) gradually decreased. The R values of all PECTFs were between 0.95 and 1.01, indicating that all PECTFs were random copolyesters. Because the boiling point of CHDM (286 °C) was much higher than that of EG (197 °C) and EG was more likely to evaporate and remove during the reaction, the CHDM content in copolymers was higher than that in feed. The mole ratio of trans-isomer in

copolyesters was basically equal to that in feed, indicating there was basically no the configuration transformation between cis and trans isomers at high temperatures in this study.

3.2. Thermal properties

Figure 7 shows DSC curves of PETF, PCTF, and PECTFs. For all polyesters, glass transition temperatures (T_g) were between 64 and 69 °C. For PECTF29, PECTF49, and PECTF77, melt crystallization temperatures (T_c) were not observed in the cooling curve and melting temperatures (T_m) were not observed in the first and second heating curves, indicating they were amorphous copolyesters. However, for PETF, a cold crystallization peak ($\Delta H_{\text{cc}} = 13.5 \text{ J/g}$) and a melting peak ($\Delta H_{\text{m}} = 16.4 \text{ J/g}$) were observed at 154.0 and 190.4 °C in the first heating curve, respectively. It was clear that PETF could crystallize slowly. Surprisingly, poly(1,4-cyclohexylenedimethylene terephthalate) (PCT) and poly(1,4-cyclohexanedimethylene furanoate) (PCF) are crystalline polymers with

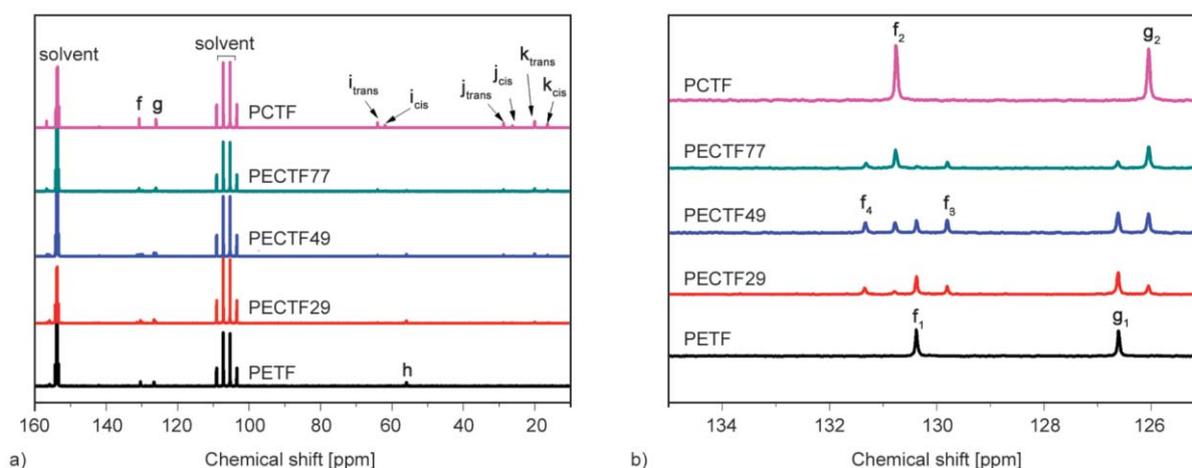


Figure 6. ^{13}C NMR spectra of PETF, PCTF, and PECTFs, a) the whole spectra, b) magnification of chemical shifts **f** and **g**.

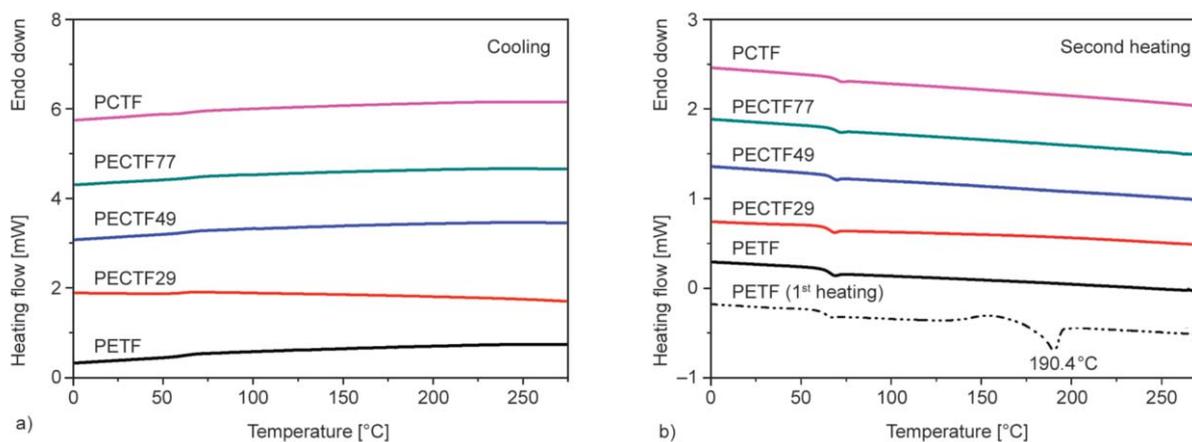


Figure 7. DSC curves of PETF, PCTF, and PECTFs, a) cooling, b) second heating.

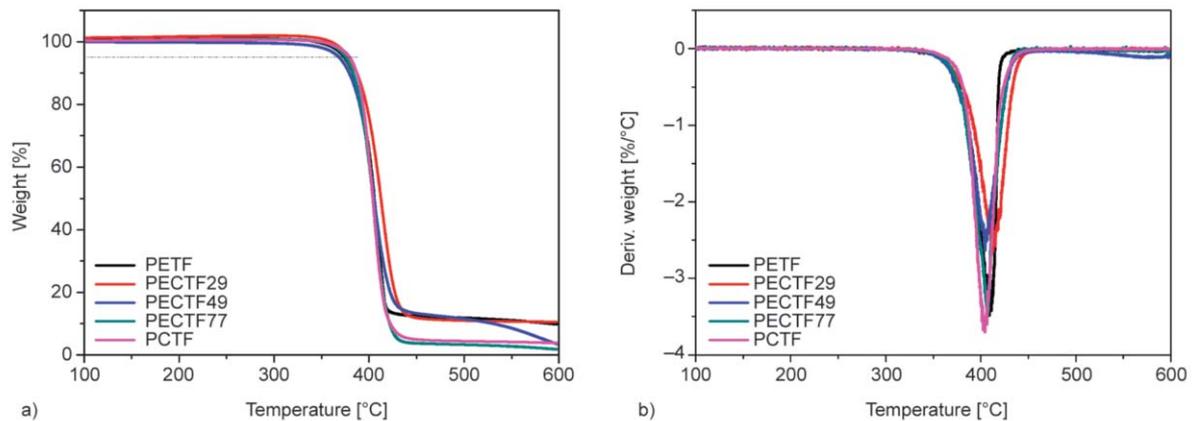


Figure 8. TGA (a) and DTG (b) curves of PETF, PCTF, and PECTFs under dynamic N₂ atmosphere.

Table 2. Thermal properties of PETF, PCTF, and PECTFs obtained by DSC and TGA.

Sample	1 st heating				2 nd heating	$T_{d,5\%}$ [°C]	$T_{d,max}$ [°C]	W_{600} [%]
	T_m [°C]	ΔH_m [J/g]	T_{cc} [°C]	ΔH_{cc} [J/g]	T_g [°C]			
PETF	190.4	16.4	154.0	13.5	64.1	374.4	409.1	9.9
PECTF29	–	–	–	–	64.3	378.3	412.8	10.5
PECTF49	–	–	–	–	65.4	368.7	406.5	3.4
PECTF77	–	–	–	–	67.7	375.6	407.5	1.8
PCTF	–	–	–	–	68.7	379.7	404.3	3.9

fast crystallization rate [20, 21], but PCTF is a amorphous polymer. Therefore, CHDM is more suitable for toughening PETF without considering the effect of crystallinity.

Figure 8 shows TGA and DTG curves of PETF, PCTF, and PECTFs under dynamic N₂ atmosphere. The temperature at 5% weight loss ($T_{d,5\%}$), the temperature at the maximum decomposition rate ($T_{d,max}$) and the residue weight at 600 °C (W_{600}) are summarized in Table 2. For all samples, $T_{d,5\%}$ and $T_{d,max}$ were all higher than 360 and 400 °C, respectively. It meant that all samples exhibited excellent thermal stabilities.

3.3. Tensile properties and dynamic mechanical behavior

Tensile tests were carried out at 25 °C at a constant stretching rate of 5 mm/min to determine the mechanical properties of PETF, PCTF, and PECTFs. Young's modulus, tensile strength, elongation at break, injection temperatures are summarized in Table 3. Figure 9 shows the characteristic tensile behavior of PETF, PCTF, and PECTFs. Figure 10 shows the β relaxation from DMA of PETF, PCTF, and PECTFs and the β relaxation temperatures are given in Table 3. For PETF, the highest tensile strength (~72 MPa) was observed. However, the nonlinear structure of TDCA

Table 3. Young's modulus, tensile strength and elongation at break of PETF, PCTF, and PECTFs.

Sample	E [MPa]	σ_m [MPa]	ϵ_b [%]	Injection temperature [°C]	Reference
PETF	1760±120	71.7±0.6	23.9±10.1	210	This work
PECTF29	1500±150	62.2±3.2	208±22	230	This work
PECTF49	1640±10	57.0±0.5	256±43	230	This work
PECTF77	1560±20	50.6±0.4	169±5	230	This work
PCTF	1350±210	49.0±0.3	176±23	240	This work
PEF	2800±120	85±9	5±1	–	[23]
PECF-59	1740±150	59±4	186±14	–	[23]
PCF	2100±200	62±4	18±4	–	[23]
PET	2297	65	173	–	[24]

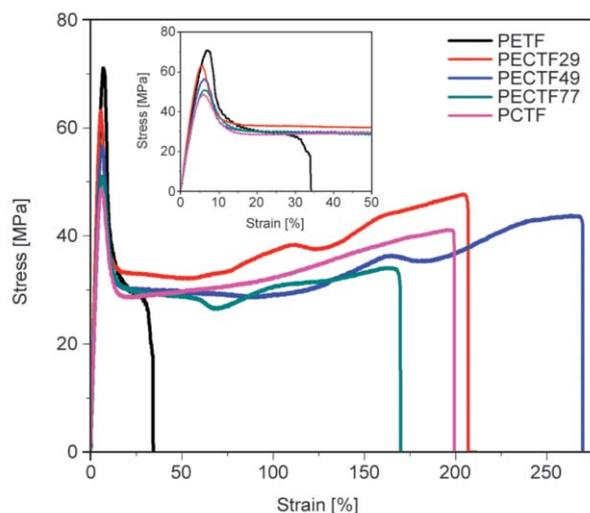


Figure 9. Stress-strain curves of PETF, PCTF, and PECTFs.

resulted in an angle of 148° between carboxylic acid carbons. Moreover, the S atom resulted in the permanent dipole. Considering the above-mentioned reasons, the thiophene ring-flipping was hindered and the low elongation at break ($\sim 24\%$) was observed for PETF. The similar phenomenon was reported for poly(ethylene furanoate) (PEF) with the similar structure [11]. Compared with PEF, PETF exhibited the lower tensile strength and the higher elongation at break, which should be attributed to the larger angle between carboxylic acid carbons (148°) and the weaker intermolecular forces caused by the S atom. However, compared with PETF, PET exhibited the lower tensile strength and the higher elongation at break, which should be attributed to an angle of 180° between carboxylic acid carbons and the benzene ring-flipping. Comparison of PETF, PEF and PET was summarized in Table 4.

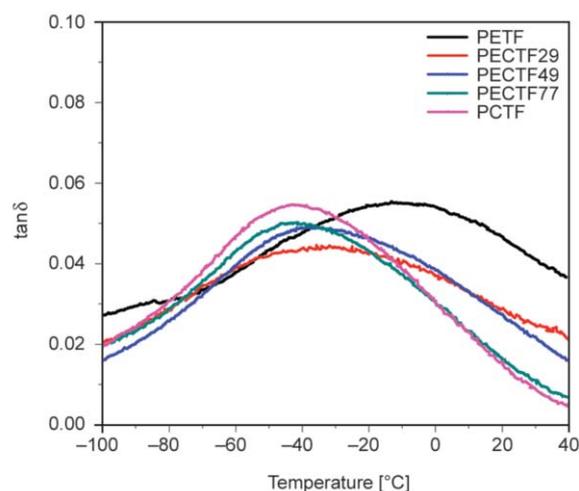
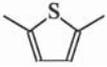
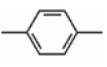


Figure 10. The β relaxation from DMA of PETF, PCTF, and PECTFs.

Table 4. Comparison of PETF, PEF and PET [11, 25, 26].

Polyesters	PETF	PEF	PET
			
An angle between carboxylic acid carbons [$^\circ$]	148	129.4	180
Ring	Polar	Polar	Nonpolar
Hindered ring-flipping?	Yes	Yes	No
Heteroatom?	S	O	No
The permanent dipole?	Yes	Yes	No

For PECTF29, PECTF49, PECTF77, and PCTF, they were ductile materials (elongation at break: 169–256%). PETF and PECTF49 with similar molecular weights and molecular weight distributions can be compared. Obviously, the difference in mechanical properties is not caused by the difference in molecular weights. The reason might be that the more units and extensive cooperative motion occurred induced by the conformational transition of cyclohexylene ring. As shown in Figure 10 and Table 5, with the increase of CHDM content, the β relaxation temperature shifted to the lower temperature, indicating that it was easier to give rise to the secondary relaxation due to the incorporation of CHDM. For another polyester poly(1,4-cyclohexylenedimethylene 1,4-cyclohexylenedicarboxylate) (PCC), the conformation transition of cyclohexylene ring was described as follows by Liu and Yee [22]: ‘The cyclohexylene ring has two most stable conformations (chair conformations). The chair-twist boat-chair conformation transition is possible in polyesters. The angle between 1,4-cyclohexylene and its neighbors changes from 180 to 114° , which induces the connected segments to translate and/or rotate. Meanwhile, the mobility of chain enhances, which leads to slide between polymer chains and shear yield.’ Compared with poly(1,4-cyclohexanedimethylene 2,5-furandicarboxylate) (PCF) with fast crystallization rate, PCTF exhibited the lower tensile strength and the higher elongation at break due to the weaker intermolecular forces

Table 5. The β relaxation peaks of PETF, PCTF, and PECTFs determined by DMA.

Samples	β relaxation peaks [$^\circ\text{C}$]
PETF	-18
PECTF29	-34
PECTF49	-46
PECTF77	-51
PCTF	-52

caused by the S atom, the larger angle between carboxylic acid carbons (148°) and the amorphous characteristic. Compared with poly(ethylene-co-1,4-cyclohexanedimethylene 2,5-furandicarboxylate)s (PECTFs) with the high content of CHDM (59%), PECTF29 exhibited better mechanical properties and higher bio-based content.

4. Conclusions

Bio-based polyesters poly(ethylene 2,5-thiophenedicarboxylate-co-1,4-cyclohexanedimethylene 2,5-thiophenedicarboxylate)s were synthesized using melt polycondensation method. Weight-average molecular weights of PETF, PCTF, and PECTFs are higher than 10 000 g/mol. For all polyesters, glass transition temperatures (T_g) were between 64 and 69 °C. PETF is a semi-crystalline polymer with slow crystallization rate. However, other copolyesters synthesized are amorphous polymers. For PETF, the highest tensile strength (~ 72 MPa) and low elongation at break ($\sim 24\%$) were observed. When the CHDM content was higher than or equal to 29%, high elongation at break ($>160\%$) was observed because the β relaxation peak shifted to the lower temperature. Additionally, compared with PEF, PETF exhibited the lower tensile strength and the higher elongation at break due to the larger angle between carboxylic acid carbons (148°) and the weaker intermolecular forces caused by the S atom. Compared with poly(1,4-cyclohexanedimethylene 2,5-furandicarboxylate) with fast crystallization rate, PCTF exhibited the lower tensile strength and the higher elongation at break due to the weaker intermolecular forces caused by the S atom, the larger angle between carboxylic acid carbons (148°) and the amorphous characteristic.

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