

Biobased Poly(ethylene-co-hexamethylene 2,5-furandicarboxylate) (PEHF) Copolyesters with Superior Tensile Properties

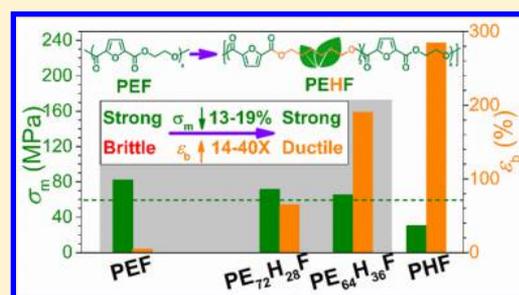
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Supporting Information

ABSTRACT: Poly(ethylene-co-hexamethylene 2,5-furandicarboxylate) (PEHF) copolyesters with high intrinsic viscosity were synthesized from 2,5-furandicarboxylic acid (FDCA), ethylene glycol (EG), and 1,6-hexanediol (HDO) through two-step melting polycondensation, characterized with ¹H NMR, DSC, WAXD, and TGA, and assessed by tensile and impact tests. The molar fraction of HF unit in PEHF (ϕ_{HF}), namely, copolymer composition, is higher than the molar fraction of HDO in the feeding diols and can be predicted empirically via Mayer–Lewis equation with apparent reactivity ratio $r_{HDO} = 4.6$ and $r_{EG} = 0.74$. All the PEHFs exhibited a single glass transition temperature and excellent thermal stability. HF-rich ($\phi_{HF} \geq 88$ mol %) PEHFs are semicrystalline but the others are almost amorphous. In comparison with PEF, PEHFs with ϕ_{HF} of 28–36 mol % possess significantly improved tensile ductility (elongation at break 54–160%) and retain high tensile modulus (2.6–2.2 GPa) and yielding strength (71–65 MPa). The tensile properties are comparable to those of bottle-grade PET.



INTRODUCTION

Poly(ethylene 2,5-furandicarboxylate) (PEF), a biobased polyester synthesized from ethylene glycol (EG) and 2,5-furandicarboxylic acid (FDCA) or its diesters, is a very promising polymer because it has not only excellent sustainability^{1–3} but also higher mechanical and gas barrier performance than poly(ethylene terephthalate) (PET),^{4,5} its petro-based counterpart. Both EG and FDCA can be synthesized from biomass like celluloses or semicelluloses as starting materials.^{6–8} Biobased EG has been industrialized and used in production of bioPET bottles, and biobased FDCA is also under the way of industrialization. In comparison with PET, PEF has higher glass transition temperature, higher stiffness and strength, lower processing temperature (in other words, lower processing energy consumption),^{4,5} and especially much higher gas barrier properties. Its O₂ and CO₂ permeability decreases by 11 and 19 times, respectively, in comparison of PET.^{9,10} Such unique performance makes it a good choice for eco-packaging application with high gas barrier demanding as well as engineering materials.

On the other hand, PEF has some inherent drawbacks in thermomechanical properties like slow melt crystallization^{11,12} and brittleness,^{13–16} which may limit its applications. Although a very recent research indicated that PEF showed high elongation at break (35–115%) after biaxial orientation,¹⁷ PEF did exhibit very limited elongation at break (1–5%)^{13–16,18–21} and impact strength (3.1 kg·cm/cm)¹³ according to many reports in literature. To toughen PEF, some PEF-based blends

or copolymers have been reported. PEF/PBS blend containing 15 wt % PBS showed highly improved impact strength of 15.5 kJ/m², but the elongation at break was still limited (6.6%).²² In contrast, multiblock copolymers like P(EF-mb-PEG) exhibited improved ductility (elongation at break of 35%) at high PEG content (60 wt %) but the tensile strength was dramatically sacrificed (15 MPa).²¹ Random copolymers with flexible diacid like poly(ethylene sebacate-co-furandicarboxylate) (PESeF) showed similar results.¹⁹ Synthesis and some properties of poly(ethylene succinate-co-furandicarboxylate) (PESF)²³ and poly(ethylene furanoate-co-ethylene terephthalate) (PEFT)²⁴ have also been reported but the mechanical properties were not clear. In comparison, random PEF copolymers with alicyclic diol like poly(ethylene-co-1,4-cyclohexanedimethylene 2,5-furandicarboxylate) (PECF) containing 32 mol % CF unit show improved elongation at break of 50% and retain quite good tensile strength (71 MPa) and modulus (2.2 GPa).¹⁴ Furthermore, with increasing the trans-isomer content of 1,4-cyclohexanedimethanol (CHDM), the tensile strength and modulus of the resulting copolymers further increased.²⁵ However, the PECFs still showed low impact strength (3.1–4.7 kg·cm/cm) in the whole composition range,¹⁵ and the comonomer CHDM is relatively expensive. PEF-based random

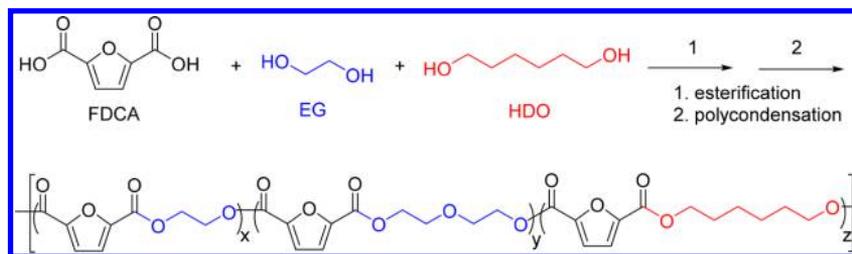
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Scheme 1. Synthesis of PEHF Copolyesters from FDCA, EG, and HDO through Two-Step Melt Polycondensation Process



copolymers with more rigid diol like poly(ethylene-*co*-2,2,4,4-tetramethyl-1,3-cyclobutylene 2,5-furandicarboxylate)s possess higher tensile modulus and strength than PEF, but the elongation at break remained almost the same as PEF.²⁰ Therefore, modified PEF materials possessing improved ductility and/or impact toughness and retaining high tensile strength and modulus at the same time are still very desired.

So far, PEF-based copolymers with aliphatic flexible diols have not been paid enough attention. Poly(ethylene-*co*-butylene 2,5-furandicarboxylate) (PEBF) is the first and sole example to date. Ma et al.²⁶ reported the synthesis, structure, and thermal properties of PEBFs, but not related to the mechanical properties. In fact, the toughness of poly(alkylene furandicarboxylate)s (PAFs) depends on the chain length of alkylene moiety. Although PEF has low ductility, PAFs with $C \geq 4$ alkylene have elongation at break higher than 130%.^{18,27–29} Among them, poly(hexamethylene 2,5-furandicarboxylate) (PHF) has been seldomly reported but it does possess high ductility (elongation at break of 210%) and reasonably good tensile strength (35.5 MPa).¹⁸ Furthermore, PHF has much better crystallizability³⁰ than PEF, and the diol monomer 1,6-hexanediol (HDO), like FDCA, can also be obtained from renewable resources such as cellulose and/or hemicellulose.^{31,32} Considering the above points, poly(ethylene-*co*-hexamethylene 2,5-furandicarboxylate) (PEHF) may be a completely biobased copolymer having complementary properties of PEF and PHF homopolymers. So far, to the best of our knowledge there is no report about the synthesis and structure–property of PEHF copolymers.

As one of a series of our works on PEF modification by copolymerization,³³ in this study PEHF copolyesters in full composition range were synthesized from FDCA, EG, and HDO through a two-step melt polycondensation process and characterized by ¹H NMR, DSC, WAXD, and TGA. The mechanical properties were assessed with tensile and notched Izod impact tests. PEHF materials with high ductility as well as high tensile strength and modulus have been successfully obtained.

EXPERIMENTAL SECTION

Materials. 2,5-Furandicarboxylic acid (FDCA, 99%), ethylene glycol (EG, 99%), and 1,6-hexanediol (HDO, 98%) were purchased from Jiaxing Ruiyuan Biotech Co. Ltd., Sigma-Aldrich, and Shanghai Aladdin Biochem Technology Co. Ltd., China, respectively. A homemade titanium–silica complex (Ti@Si, Ti 1 wt % or 0.21 mmol Ti/g) prepared via sol–gel method was used as the catalyst for polyester synthesis. Phenol, 1,1,2,2-tetrachloroethane (TCE), deuterated trifluoroacetic acid (TFA-*d*₁) of analytical grade, and tetramethylsilane (TMS) were all purchased from Sinopharm Chem Agents Co. Ltd., China. All the chemicals were used as received without any purification.

Synthesis. The poly(ethylene-*co*-hexamethylene 2,5-furandicarboxylate) (PEHF) copolyesters were synthesized from FDCA, EG, and HDO via two-step melt polycondensation process. The reaction was conducted in a 250 mL four-necked round-bottom flask equipped with a mechanical stirrer, nitrogen inlet, and reflux condenser. The diols (EG + HDO) and diacid (FDCA) at a diol/diacid molar ratio of 2.0 and homemade catalyst Ti@Si (0.1 wt % of FDCA) were charged after the flask was purged with nitrogen for a period of time. During the esterification stage, the reaction was performed at 190 °C for 1 h and then held at 200 °C until about 95% of the theoretical amount of water was distilled out. Then, the polycondensation reaction was conducted at 230 °C for 1 h and 240 °C for 2–4 h under reduced pressure of about 100 Pa. The reaction was considered as completion when clear Weissenberg effect emerged. The same procedure was also adopted for the synthesis of PEF and PHF except longer polycondensation time was needed for PHF. At last, the resulting copolyesters were dried at 60 °C in vacuum for characterization without purification.

Characterization. Intrinsic viscosity ($[\eta]$) of the (co)-polyesters was measured with an semiautomatic viscosity tester (ZONWON IVS300, China) equipped with a Ubbelohde viscometer. Each sample was measured at 25 °C in a phenol/TCE (3/2, w/w) mixed solvent with the concentration of 5 g/dL.

¹H NMR spectra of the (co)polyesters were recorded on Bruker AC-80 (400 M), using TFA-*d*₁ as the solvent and TMS as the internal reference.

Differential scanning calorimetry (DSC) analysis was performed on a TA-Q200 thermal analyzer (TA Instrument, U.S.A.) with standard heating–cooling–heating program. Both the heating and cooling rate were 10 °C/min, and the isothermal time was 5 min. For all samples except PEF, the temperature ranges for the first heating, cooling, and second heating scans were 40–250 °C, 250–90 °C and –90–250 °C, respectively. For PEF, the corresponding temperature ranges were 40–250 °C, 250–30 °C, and 30–250 °C, respectively.

Thermal decomposition behavior of the (co)polyesters was determined by thermogravimetric analysis (TGA) on a TA Q500 analyzer (TA Instrument, U.S.A.). Samples of about 3 mg were measured from 50 to 600 °C at a heating rate of 10 °C/min under nitrogen atmosphere.

The tensile properties were examined using a Zwick Roell Z020 (Zwick, Germany) testing machine at room temperature according to ASTM D638 with a crosshead speed of 10 mm/min. Dumbbell-shaped specimens with dimensions of 75 mm (length) × 4 mm (neck width) × 2 mm (thickness) were prepared by a HAAKE MiniJet injection molding machine and then conditioned at room temperature for at least 48 h before

Table 1. Synthetic Conditions^a and Macromolecular Characteristics of PEF, PHF, and PEHF Copolyesters

run	ϕ_{HDO}^b (mol %)	C_{es}^c (%)	t_{mp}^d (h)	$[\eta]^e$ (dL/g)	¹ H NMR			
					ϕ_{HF}^f (mol %)	ϕ'_{HF}^g (mol %)	ϕ_{DEGF}^h (mol %)	ϕ'_{DEGF}^i (mol %)
1	0	97	3	0.82	0	0	5.2	5.2
2	10	93	4	0.76	19.3/20.4	18.7	3.3	4.1
3	16	96	4	0.85	28.3/28.5	27.5	3.1	4.2
4	20	95	4	0.82	35.9/34.3	35.0	2.5	4
5	30	94	3	0.96	52.3/51.7	51.3	1.9	3.9
6	40	94	3	1.05	65.9/63.3	64.7	1.8	5.3
7	60	94	2	1.12	87.8/86.3	86.8	1.2	9.8
8	100	92	5	0.72	100	100	0	

^a(1) Esterification: Ti@Si, 0.1 wt % based on FDCA was used as catalyst; (EG+HDO)/FDCA molar ratio was 2.0; 190 °C for 1 h, and then 200 °C for 3 h. (2) Polycondensation: no additional catalyst was added; 230 °C for 1 h and then at 240 °C for t_{mp} . ^bMolar percentage of HDO in the diol (EG+HDO) feed. ^cEsterification rate, equal to the conversion of carboxyl group, calculated from the yield of water. ^dPolycondensation time needed for clear Weissenberg effect emerged at 240 °C and stirring rate under 50 rpm. ^eIntrinsic viscosity measured at 25 °C using the phenol/TCE (3/2, w/w) mixed solvent. ^fMolar percentage of HF unit in the copolyester calculated with eqs 3 and 4, respectively. The value “a/b” represented that a and b were calculated with eqs 3 and 4, respectively. ^gMolar percentage of HF unit in the copolyester calibrated with eq 5. ^hMolar percentage of DEGF unit in the copolyester calculated with eq 2. ⁱMolar percentage of DEGF unit in the sum of EF and DEGF units calculated with eq 6.

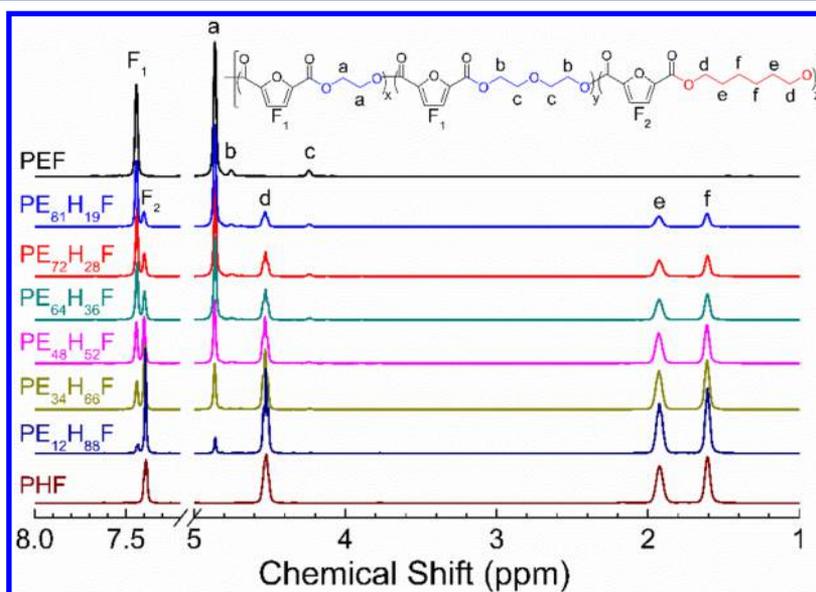


Figure 1. ¹H NMR spectra of PEF, PHF and PEHF copolyesters. Note: chemical shift at 11.6 ppm for solvent TFA-*d*₁.

testing. For each sample, at least five specimens were tested. All the specimens were tested at a crosshead speed of 10 mm/min.

Notched Izod impact testing was done using a CEAST Resil impact tester (CEAST, Italy) with a pendulum of 5.5 J according to ASTM D256. The samples with dimensions of 80 mm (length) × 10 mm (width) × 4 mm (thickness) were prepared by a HAAKE MiniJet injection molding machine. All samples were notched and conditioned at room temperature for at least 48 h before testing. The result for each sample was averaged from the measurement of at least five specimens.

■ RESULT AND DISCUSSION

Synthesis and Structure Characterization. PEF, PHF, and PEHF copolyesters with different compositions (expressed with molar percentage of hexamethylene 2,5-furandicarboxylate (HF) unit, ϕ_{HF}) were synthesized via the two-step melt polycondensation process using various HDO feeding ratios, ϕ_{HDO} , as shown in Scheme 1. The synthetic conditions and results are listed in Table 1. PEF with high intrinsic viscosity ($[\eta]$) of 0.82 dL/g was synthesized in this study, which is

among the best results reported in the literature.^{13,14,18,34–36} The copolyesters also show high $[\eta]$, varying from 0.76 to 1.12 dL/g. Interestingly, the intrinsic viscosity positively correlates with the HDO feeding ratio. At higher ϕ_{HDO} , higher intrinsic viscosity was obtained even at shorter polycondensation time (t_{mp}). This result suggests that the presence of HDO is advantageous to the molecular weight growth of the copolyesters and/or the molecular weight dependence of $[\eta]$ of the PEHF copolyesters changed with their composition. However, in comparison with PEF and PEHF copolyesters, it is more difficult to synthesize high molecular weight PHF because of low volatilization of HDO.²⁹ In a previous report, PHF with $[\eta]$ of 0.47 dL/g was synthesized.³⁰ In this study, PHF with $[\eta]$ as high as 0.72 dL/g was successfully synthesized, possibly due to the high reactivity of the catalyst as evidenced in our previous study.³³ The lower $[\eta]$ of PHF indicates that the volatility of EG is an important factor for synthesizing high intrinsic viscosity PEHF copolyesters.

The chemical structure and composition of the (co)-polymers were characterized with ¹H NMR, as shown in

Figure 1. For PEF, the peaks at 7.44 and 4.86 ppm are attributed to CH (F_1) in furan ring and CH_2 (a) in EG unit, respectively. The small chemical shifts at 4.75 and 4.24 ppm are assigned to the outer CH_2 (b) and inner CH_2 (c) in diethylene glycol furandicarboxylate (DEGF) unit formed by the etherification side reaction during the polycondensation, as confirmed by Wu et al.¹¹ For PHF, the peak for the CH (F_2) in furan ring shifts from 7.44 to 7.40 ppm, resulting from different chemical environment in HF unit as compared with EF or DEGF unit. The chemical shifts at 4.53, 1.93, and 1.61 ppm are attributed to the CH_2 (d) close to the ester bond, middle CH_2 (e) and central CH_2 (f) of HDO unit. For PEHF copolyesters, all the signals from the two homopolymers, PEF and PHF, can be found, and the peak areas of EF (F_1 , a) and DEGF unit (b, c) decreases while those of HF unit (F_2 , d, e, f) increases with increasing ϕ_{HF} . Therefore, the PEHF copolyesters with expected structure containing EF, DEGF and HF repeat units are successfully synthesized.

From the 1H NMR spectra, the molar percentage of the three repeat units, namely, ϕ_{EF} of EF, ϕ_{DEGF} of DEGF, and ϕ_{HF} of HF, can be calculated using eqs 1~3

$$\phi_{EF} \text{ (mol\%)} = \frac{I_a}{I_a + I_c + I_f} \times 100 \quad (1)$$

$$\phi_{DEGF} \text{ (mol\%)} = \frac{I_c}{I_a + I_c + I_f} \times 100 \quad (2)$$

$$\phi_{HF} \text{ (mol\%)} = \frac{I_f}{I_a + I_c + I_f} \times 100 \quad (3)$$

$$\phi_{HF} \text{ (mol\%)} = \frac{I_{E_2}}{I_{F_1} + I_{E_2}} \times 100 \quad (4)$$

where I_a , I_c , and I_f are the peak areas of chemical shifts a, c, and f, respectively. The value of ϕ_{HF} can also be calculated with eq 4. The results are listed in Table 1. The two series of ϕ_{HF} results agree well with each other, evidencing the correct attribution of the chemical shifts. Normally, the molar percentage of HF unit, ϕ_{HF} , is used to express the copolyester composition. Therefore, PEHF copolyester containing $x = \phi_{HF}$ mol % of HF unit is symbolized as $PE_{100-x}H_xF$. However, it should be calibrated with eq 5 to be ϕ'_{HF} when comparing the content of HF unit in the copolyester with HDO content in diol feed (ϕ_{HDO}) because two EG moieties exist in DEGF unit. Clearly, ϕ'_{HF} is slightly lower than ϕ_{HF} . It can be seen that the ϕ'_{HF} value is much higher than the corresponding ϕ_{HDO} . A similar result was also reported in the synthesis of PEBF copolyesters and was attributed to higher reactivity of BDO than EG.²⁶ For PEHF copolyesters, the less volatility and the higher reactivity of HDO than EG both contributed to the higher content of HF unit in the copolyester chain. In order to obtain a quantitative empirical correlation between ϕ'_{HF} and ϕ_{HDO} , the classic Mayo–Lewis equation which is widely used in calculating the composition of free radical copolymers was borrowed here to fit our data. As shown in Figure 2, Mayo–Lewis equation fits the ϕ'_{HF} – ϕ_{HDO} data quite well and the apparent reactivity ratios of HDO and EG are supposed to be 4.60 and 0.74, respectively. From this result, it is clear that HF unit has strong homopolymerization but EF unit has strong copolymerization tendency, which leads to the higher HF unit content in the PEHF copolyesters

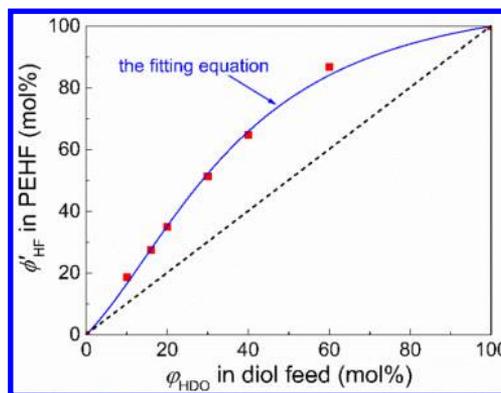


Figure 2. Dependence of the copolymer composition of PEHF copolyesters (ϕ'_{HF} , molar percentage of HF unit in copolyester) on the monomer composition (ϕ_{HDO} , molar percentage of HDO in diol feed). Red dots, experimental data; solid line, fitting curve by Mayo–Lewis equation: $F_1 = \frac{r_1^2 + f_1 f_2}{r_1^2 + 2f_1 f_2 + r_2^2}$, $F_1 = \phi'_{HF}$, $f_1 = \phi_{HDO}$, $f_2 = \phi_{EG} = 1 - \phi_{HDO}$.

$$\phi'_{HF} \text{ (mol\%)} = \frac{I_f}{I_a + 2I_c + I_f} \times 100 \quad (5)$$

The molar percentage of DEGF unit ϕ_{DEGF} , along with ϕ_{EF} , decreases with ϕ_{HDO} . In order to reflect the selectivity of etherification side reaction during PEHF synthesis, ϕ'_{DEGF} , the molar percentage of DEGF unit in the sum of EF and DEGF units, was calculated with eq 6. The ϕ'_{DEGF} value keeps almost unchanged at ϕ_{HDO} no more than 30 mol % but unexpectedly increases at higher ϕ_{HDO} . The reason is not clear yet and needs further study

$$\phi'_{DEGF} \text{ (mol\%)} = \frac{I_c}{I_a + I_c} \times 100 \quad (6)$$

■ THERMAL TRANSITION PROPERTIES

Thermal transition behaviors of PEF, PHF, and PEHF copolyesters were recorded with DSC. The cooling and second heating scans at 10 °C/min are shown in Figure 3, and

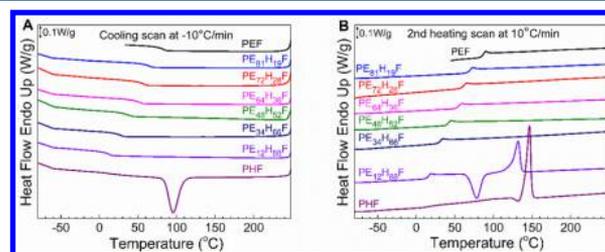


Figure 3. DSC curves of PEF, PHF, and PEHF copolyesters: (A) cooling scan at 10 °C/min; (B) second heating scan at 10 °C/min.

the thermal transition properties including glass transition temperature (T_g), cold crystallization temperature (T_{cc}) and enthalpy (ΔH_{cc}), melt crystallization temperature (T_c) and enthalpy (H_c), and melting temperature (T_m) and enthalpy (ΔH_m) are listed in Table 2. The PEF sample manifests poor crystallizability only showing small to tiny cold crystallization peak ($\Delta H_{cc} = 5.4$ J/g, $T_{cc} = 175.9$ °C) and melting peak ($\Delta H_m = 5.9$ J/g, $T_m = 211.3$ °C) in the first scan (Figure S1) but no peak is observed in both cooling and second heating scan. PEF crystallizes slowly possibly because of its restricted molecular

Table 2. Thermal Properties of PEF, PHF, and PEHF Copolyesters

sample	1st heating		cooling		2nd heating					TGA ^a	
	T_m (°C)	ΔH_m (J/g)	T_c (°C)	ΔH_c (J/g)	T_g (°C)	T_{cc} (°C)	ΔH_{cc} (J/g)	T_m (°C)	ΔH_m (J/g)	$T_{d,5}$ (°C)	$T_{d,max}$ (°C)
PEF	211.3	5.9	nd	nd	88	nd	nd	nd	nd	376	416
PE ₈₁ H ₁₉ F	nd	nd	nd	nd	70	nd	nd	nd	nd	373	425
PE ₆₄ H ₃₆ F	nd	nd	nd	nd	56	nd	nd	nd	nd	365	406
PE ₄₈ H ₅₂ F	nd	nd	nd	nd	42	nd	nd	nd	nd	365	404
PE ₃₄ H ₆₆ F	nd	nd	nd	nd	32	nd	nd	nd	nd	366	398
PE ₁₂ H ₈₈ F	131.7	36.9	nd	nd	17	78.6	33.1	132.1	33.5	367	400
PHF	148.0	52.7	95.2	54.9	15	nd	nd	146.8	50.6	367	399

^aN₂, 10 °C/min.

chain motion.⁵ The presence of relatively high content of DEGF unit in PEF chain disturbs the structural regularity and therefore further slows down the crystallization rate. In contrast, PHF is a semicrystalline polymer with superior crystallizability because of its high chain flexibility coming from the hexamethylene moiety. PHF melt shows strong crystallization peak at 95.2 °C with ΔH_c of 54.9 J/g in the cooling scan. Because of the previous full melt crystallization, no cold crystallization but clear melting (146.8 °C, 50.6 J/g) occurs in the second heating scan. The minor cold crystallization peak (132.1 °C, 1.5 J/g) just before the melting peak is associated with melting–recrystallization of defective lamellae. The PEHF copolyesters show weaker crystallizability than corresponding homopolymers because the presence of co-units (HF in EF-rich and EF in HF-rich copolyesters) disturbs the regular chain structure of the respective homopolymers. Because of very weak crystallizability of PEF but superior crystallizability of PHF, PEHFs containing 19–66 mol % HF unit are almost amorphous polymers, showing neither melt/cold crystallization nor melting in all DSC scans, but PEHFs containing 88 mol % or more HF unit retain quite good cold crystallizability (78.6 °C, 33.1 J/g) and melting (132.1 °C, 33.5 J/g) though no melt crystallization is observed in the cooling scan.

Having high chain rigidity and high molecular weight, the PEF sample showed high T_g of 89 °C as well as high T_m . In contrast, PHF has a much lower T_g of 15 °C because of its superior chain flexibility. The T_g value of PHF is higher than that (7 °C) reported by Papageorgiou et al.³⁰ but lower than that (28.1 °C) reported by Jiang et al.,¹⁸ mainly due to different molecular weights (0.47 dL/g,³⁰ 0.72 dL/g (this study), 1.04 dL/g¹⁸). Because of the rapid melt crystallization of PHF, such a T_g value obtained from semicrystalline PHF sample is overestimated to some extent. It is remarkable from Figure 3B that all the PEHF copolyesters have a single ϕ_{HF} -dependent T_g , and the T_g decreases with increasing ϕ_{HF} , suggesting the random structure of the PEHF copolyesters. Furthermore, the T_g values of PEHF copolyesters agree well with the values calculated from the well-known Fox equation, as shown in Figure 4, which further indicates the random structure of PEHFs.

Crystal Structure. The crystal structure of PEF, PE₁₂H₈₈F copolyester, and PHF were investigated with WAXD. Before testing, PEF was isothermally crystallized at 150 °C for 3 h after quenching from melt, the PE₁₂H₈₈F copolyester and PHF were kept at room temperature for at least 24 h after quenching from melt. The results are shown in Figure 5. As for PEF, different experimental condition leads to different crystal structure. It is well-known that the stable triclinic α -PEF crystalline phase and the less stable monoclinic α' -PEF crystalline phase can be formed at high-crystallization temper-

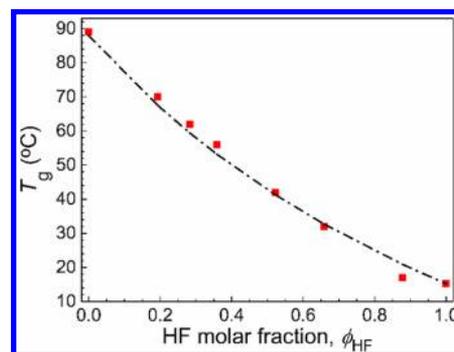


Figure 4. Composition dependence of the glass transition temperature (T_g) of PEHF copolyester. The dashed line shows the values calculated using the Fox equation: $1/T_g = w_{HF}/T_{g,PHF} + (1 - w_{HF})/T_{g,PEF}$.

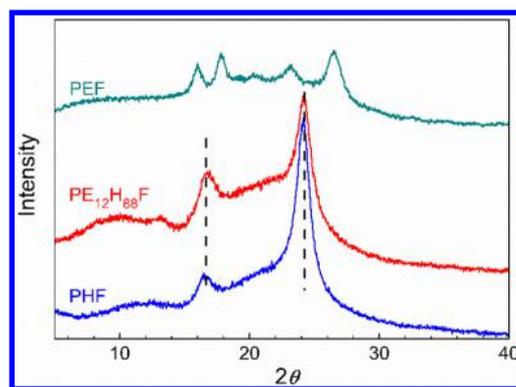


Figure 5. WAXD patterns of PEF, PE₁₂H₈₈F copolyester, and PHF.

ature ($T_c > 170$ °C) and low-crystallization temperature ($T_c < 170$ °C), respectively³⁷ and the monoclinic β -PEF crystalline phase can be obtained after solvent-induced crystallization treatment.³⁸ Very recently, Miani et al. re-examined the crystal structure of PEF under various conditions.³⁹ According to their report, the cell parameters of the monoclinic α' -PEF crystalline phase are $a = 5.912$ Å, $b = 6.91$ Å, $c = 19.73$ Å, $\alpha = 90^\circ$, $\beta = 90^\circ$, and $\gamma = 104.41^\circ$. In this study, the PEF sample exhibited five diffraction peaks at $2\theta = 16^\circ$, 17.8° , 20.3° , 23.2° , 26.5° attributed to α' crystal structure of PEF reported previously.^{37–39} PHF displayed two sharp peaks at 16.47° and 24.15° , which is in accordance with the result reported by Jiang et al.¹⁸ For the PE₁₂H₈₈F copolyester, the similar crystal pattern with PHF is observed, indicating that the crystal structure of PE₁₂H₈₈F copolyester is the same as PHF, and the EF units are excluded from the crystals formed by HF units. In addition, weaker intensity of WAXD patterns is observed for

PE₁₂H₈₈F in comparison with PHF, suggesting the lower crystallinity, which agrees well with the DSC results.

Thermal Stability. The TGA curves of PEF, PHF, and PEHF copolyesters are shown in Figure 6. The temperature at

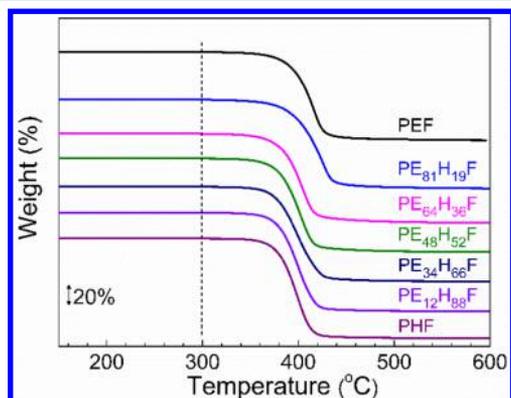


Figure 6. TGA curves of PEF, PHF, and PEHF copolyesters. (N₂, 10 °C/min).

5% weight loss ($T_{d,5}$) and the maximum weight loss rate ($T_{d,max}$) are summarized in Table 2. Clearly, all the (co)polyesters show no thermal deposition before 300 °C, indicating excellent thermal stability. All of them exhibit a single degradation step, suggesting the similar mechanism of thermal decomposition. According to the study of the decomposition mechanism of poly(alkylene 2,5-furandicarboxylate)s (PAFs) reported by Terzopoulou et al.,⁴⁰ the number of methylene groups of the repeat units of PAFs has little impact on the thermal decomposition mechanism of these polyesters. The β -hydrogen bond scission and α -hydrogen bond and homolytic chain scission are the two main pathways during the thermal decomposition of PAFs. The former leads to the carboxyl and vinyl end groups, and the latter leads to the aldehydes and hydroxyl end groups. In addition, PHF shows slightly lower $T_{d,5}$ (367 °C vs 376 °C) and $T_{d,max}$ (399 °C vs 416 °C) than PEF, which agrees well with the conclusion drawn by previous reports that the thermal stability of PAFs decreases with the increasing of the number of methylene repeating units.^{41,42} In conclusion, the composition dependences of thermal decomposition temperature of the PEHF copolyesters are slight. Both $T_{d,5}$ and $T_{d,max}$ decrease slightly with increasing ϕ_{HF} .

Mechanical Properties. Finally, the mechanical performance of PEF, PHF, and PEHF copolyesters was assessed with tensile and impact tests. Typical tensile curves are shown in Figure 7. The Young's modulus (E), tensile stress at yield and break (σ_y , σ_b) and elongation at yield and break (ϵ_y , ϵ_b) are listed in Table 3. The composition dependences of the tensile properties are displayed in Figure 8. In comparison with the PEF synthesized from dimethyl furandicarboxylate in our previous study,³³ the PEF synthesized from FDCA in this study has higher DEGF content (5.2 mol % vs 2.3 mol %) but exhibits almost unchanged elongation at break (4% vs 3%), tensile modulus (3.3 vs 3.4 GPa) and strength at break (82 vs 84 MPa). The modulus and strength are comparable to the best results reported in previous literature^{14,20,21} and the brittleness is obvious. Brittle failure is also found for PE₈₁H₁₉F. It displays decreased tensile modulus (2.8 GPa) and breaking strength (66 MPa) but unchanged elongation at break (3%) when compared with PEF, indicating that ϕ_{HF} of 19 mol % is

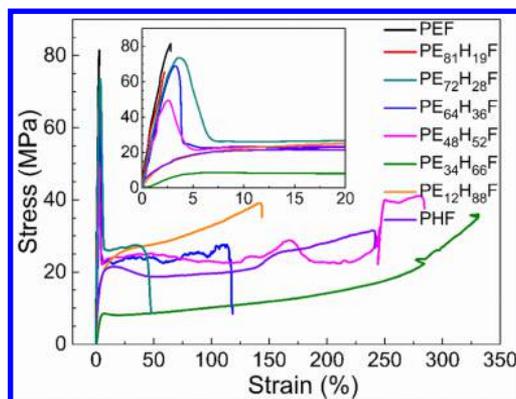


Figure 7. Typical stress–strain curves of PEF, PHF, and PEHF copolyesters.

not enough to significantly modify the tensile toughness of PEF.

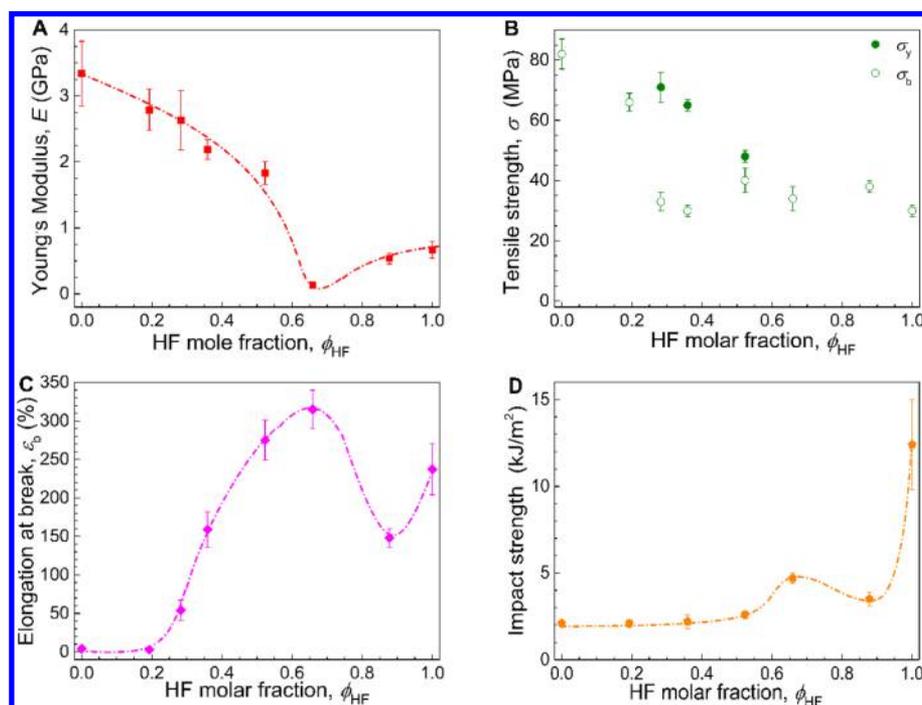
Different from PE₈₁H₁₉F, clear yielding/necking phenomenon and significantly improved elongation at break (54–275%) are observed for PEHF copolyesters with ϕ_{HF} of 28–52 mol %. Very importantly, sufficiently high tensile modulus (2.6–1.8 GPa) and maximum strength (yielding strength) (71–48 MPa) are still retained for these copolyesters at the same time. Particularly, PE₇₂H₂₈F and PE₆₄H₃₆F show tensile performance comparable to bottle-grade PET.⁴³ Furthermore, these PEHF copolyesters have better tensile toughness, strength, and modulus when compared with other PEF-based copolyesters containing flexible moieties like PSEFs¹⁹ and P(EG-*mb*-PEG).²¹ From the fact that sebacic acid has more flexible (CH₂)_n segments than HDO, it can be deduced that copolymerization with flexible diol comonomer instead of diacid comonomer seems to be advantageous to reach more balanced tensile performance, or in other words, to retain higher strength and modulus. The possible reason may be that more furan ring structure can be retained in PEF-based copolyesters with diols.

At higher ϕ_{HF} , typical tensile characteristic of elastomer is observed for PEHF copolyesters. For PE₃₄H₆₆F copolyester, the elongation at break further increases to 315%, but the tensile modulus sharply decreases to 133 MPa and breaking strength decreases to 34 MPa. However, for an elastomer, the modulus and strength are still very high. In comparison with PE₃₄H₆₆F, PE₁₂H₈₈F shows higher tensile modulus (537 MPa) and breaking strength (38 MPa) but lower elongation at break (148%) due to its crystallization proved by DSC. In addition, the PHF homopolymer exhibits tensile modulus of 666 MPa, breaking strength of 30 MPa and an elongation at break of 237%. The results are consistent with the tensile properties of PHF reported by Jiang et al.¹⁸

The impact toughness of PEHF copolyesters was examined by the notch impact test. The impact strength values are listed in Table 3 and plotted with composition in Figure 8D. It can be seen that PHF has much better impact toughness than PEF, exhibiting much higher impact strength (σ_{imp} , 12.4 ± 2.6 kJ/m² vs 2.1 ± 0.1 kJ/m²). To the best of our knowledge, this is the first and sole report about the impact strength of PHF. The impact strength of PEHF copolyesters displays an upward trend with the increasing ϕ_{HF} but its composition dependence is quite different from that of elongation at break. The impact strength is not clearly enhanced until the ϕ_{HF} reaches 52 mol % but great improvement in tensile ductility was realized

Table 3. Young's Modulus (E), Tensile Strength at Yield (σ_y) and Break (σ_b), Elongation at Yield (ϵ_y) and Break (ϵ_b), and Notch Impact Strength (σ_{imp}) of PEF, PHF, and PEHF Copolyesters

sample	E (GPa)	σ_y (MPa)	σ_b (MPa)	ϵ_y (%)	ϵ_b (%)	σ_{imp} (kJ/m ²)
PEF	3.34 ± 0.49		82 ± 5		4 ± 1	2.1 ± 0.1
PE ₈₁ H ₁₉ F	2.79 ± 0.31		66 ± 3		3 ± 1	2.1 ± 0.2
PE ₇₂ H ₂₈ F	2.63 ± 0.45	71 ± 5	33 ± 3	3.7 ± 0.3	54 ± 13	
PE ₆₄ H ₃₆ F	2.19 ± 0.15	65 ± 2	30 ± 2	3.4 ± 0.4	159 ± 23	2.2 ± 0.4
PE ₄₈ H ₅₂ F	1.83 ± 0.17	48 ± 2	40 ± 4	2.7 ± 0.2	275 ± 26	2.6 ± 0.2
PE ₃₄ H ₆₆ F	0.133 ± 0.027		34 ± 4		315 ± 25	4.7 ± 0.3
PE ₁₂ H ₈₈ F	0.537 ± 0.082		38 ± 2		148 ± 12	3.5 ± 0.4
PHF	0.666 ± 0.124		30 ± 2		237 ± 33	12.4 ± 2.6

**Figure 8.** Composition dependences of the Young's modulus (A), tensile strength (B), elongation at break (C), and notch impact strength (D) of PEF, PHF, and PEHF copolyesters.

earlier at ϕ_{HF} of 28 mol %. More flexible units are demanded for the brittle-toughness transition than the brittle-ductility transition. Similar result has also been found in our previous research of P(EF-mb-PTMG) multiblock copolymers.³³ In addition, it can be seen that the impact strength of PE₁₂H₈₈F (3.5 ± 0.4 kJ/m²) is lower than that of PE₃₄H₆₆F (4.7 ± 0.3 kJ/m²) though the former has higher ϕ_{HF} value. Clearly, this is related to the better crystallizability of PE₁₂H₈₈F. High crystallinity and large size crystals often leads to the weakened impact toughness.^{44,45}

CONCLUSIONS

High molecular weight poly(ethylene-hexamethylene furandicarboxylate) (PEHF) copolyesters in full composition range were successfully synthesized from FDCA, EG, and HDO. The molar fraction of HF repeat unit in the copolyesters (ϕ_{HF}) is clearly higher than the molar fraction of HDO in the diol feed (ϕ_{HDO}). They can be correlated with an empirical equation, Mayo–Lewis equation, with apparent reactivity ratio $r_{\text{HDO}} = 4.6$ and $r_{\text{EG}} = 0.74$. HF-rich ($\phi_{\text{HF}} \geq 88$ mol %) PEHF copolyesters are semicrystalline but the others are almost amorphous polymers. All the copolyesters have a single T_g which decreases with increasing ϕ_{HF} and show excellent

thermal stability. The amorphous copolyesters show decreased tensile modulus and strength but increased elongation at break and impact strength with increasing ϕ_{HF} . Among them, the PEHFs with ϕ_{HF} of 28–36 mol % possess significantly improved tensile ductility (elongation at break 54–160%) without greatly sacrificing their tensile modulus (2.6–2.2 GPa) and yielding strength (71–65 MPa). The tensile performance is comparable to that of bottle-grade PET. The superior mechanical properties and potential 100% biobased production of these PEHF copolyesters will endow them potential for practical applications in eco-packaging industry.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.iecr.8b03204.

Figure S1: First heating scan of PEF, PHF and PEHF copolyesters. Table S1: thermal transition properties of PEF, PHF, and PEHF copolyesters at first heating scan (PDF)

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Notes

The authors declare no competing financial interest.

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