



Modification of poly(ethylene 2,5-furandicarboxylate) with aliphatic polycarbonate diols: 1. Randomized copolymers with significantly improved ductility and high CO₂ barrier performance

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ABSTRACT

Poly(ethylene 2,5-furandicarboxylate) (PEF) is a very promising biobased polymer possessing very high mechanical strength, rigidity and gas barrier performance. But its poor ductility and toughness may limit its applications. In this study, PEF-based copolymers with high intrinsic viscosity were successfully synthesized via melt polycondensation of dimethyl 2,5-furandicarboxylate (DMFD) and ethylene glycol in the presence of a copolycarbonate diol (PpEHC diol) as produced from 1,5-pentylene diol (PeDO), 1,6-hexylene diol (HDO) and dimethyl carbonate, and characterized with ¹H NMR, ¹³C NMR, DSC, TGA, tensile, impact and gas barrier testing. The products were “randomized” as a result of ester-carbonate exchange reaction occurring along melt polycondensation, and therefore became amorphous copolymers possessing composition-dependent physico-mechanical properties which can be tunable from rigid-to-ductile thermoplastics to thermoplastic elastomers. Particularly, the copolymers with ϕ_{PpEHC} of 25 wt% and 30 wt% are thermoplastics possessing greatly improved ductility (elongation at break up to 194%) and CO₂ barrier performance higher than poly(ethylene terephthalate) (PET; BIF_{CO2} 3.6–2.8), and retaining high tensile modulus (2.2–1.9 GPa) and yielding strength (69–58 MPa) comparable to the bottle-grade PET. In comparison, the copolymer with ϕ_{PpEHC} of 40 wt% behaves as a high performance thermoplastic elastomer with excellent gas barrier performance as well as high tensile strength (23 MPa).

1. Introduction

Poly(ethylene terephthalate) (PET) is the largest in output and the most widely used polyester material. It possesses good physical performance, optical clarity, processability as well as low cost, and has been widely used for fibers, bottles, engineering and package materials [1]. So far, the production of PET is mainly from non-renewable petroleum resources [2,3]. Moreover, although various techniques have been developed to improve its gas barrier properties [4–7], PET still underperforms in packaging applications with high gas barrier demanding. As an interesting biobased polyester, poly(ethylene 2,5-furandicarboxylate) (PEF) synthesized from biobased 2,5-furandicarboxylic acid or its diester and ethylene glycol possesses not only huge resource and environmental benefits [8] but also better thermal and mechanical performance [9] and superior gas barrier properties. It has been reported that the O₂ and CO₂ permeability of PEF decrease by

5.5–11 [10,11] and 13–19 folds [11,12] respectively in comparison with PET. Such high performances make PEF a competitive candidate for eco-packaging applications in oxygen sensitive foods and beverages which demand high gas barrier performance and high mechanical properties.

However, PEF is a brittle material [9,13,14], showing a very limited elongation at break (1–5%) [11,13–18] and impact strength (2.1–2.5 kJ/m² [19,20] or 3.1 kg.cm/cm [13]), which hinders its practical applications. To improve the toughness of PEF, biaxial-orientation [21], blending [20,22,23] and copolymerization [11,13,15–17,19,24–29] of PEF have been reported in recent years. van Berkel et al. [21] reported that the elongation at break of PEF was improved to 30–110% after biaxial orientation under areal stretch ratio of 3.5–5.0 at 105 °C. Chen et al. [20] reported that the impact strength of PEF was enhanced from 2.5 kJ/m² to 15.5 kJ/m² after melt blending with 15 wt% PBS, but at the same time, the blend still showed

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elongation at break as low as 6.6%.

PEF-based random copolymers have attracted much attention in recent years. Several diacids or diols have been employed as comonomers to enhance the ductility and/or impact toughness of PEF. Copolymerizing with aliphatic or alicyclic diacids such as sebacic acid [15], dodecanedioic acid [28] and 1,4-cyclohexanedicarboxylic acid [26] can improve the ductility to some extent at relatively high comonomer content, but often lead to clear sacrifice of tensile strength and modulus and glass transition temperature. Random PEF copolyesters with ϵ -caprolactone also showed similar performance-composition dependence [27]. In contrast, aliphatic or alicyclic diols behaved much better in modifying PEF. Wang et al. [11] reported that poly(ethylene-co-1,4-cyclohexanedimethylene 2,5-furandicarboxylate) (PECF) showed improved elongation at break (50%-186%) at 32–76 mol% CF content, and at the same time, retained high T_g , tensile modulus (2.2–1.7 GPa), strength (71–59 MPa) and gas barrier properties. Furthermore, these properties can be tuned or even enhanced by the trans/cis ratio of the comonomer, 1,4-cyclohexanedimethanol [25]. In our recent studies, poly(ethylene-co-hexylene 2,5-furandicarboxylate) (PEHF) [19] and poly(ethylene-co-pentylene 2,5-furandicarboxylate) (PEPeF) [24] showed mechanical properties comparable to or even better than PECF at lower comonomer content. Particularly, incorporating 18 mol% 1,5-pentanediol into PEF resulted in a high performance copolymer possessing greatly improved ductility (elongation at break 115%), and at the same time, retaining unchanged yielding strength (83 MPa) and modulus (3.3 GPa), high O_2 barrier property (4.8 folds to PET) and T_g (ca. 75 °C).

PEF-based multiblock copolymers such as PEF-mb-PEG [16] (where PEG stands for poly(ethylene glycol) and PEF-mb-PTMG [30] (PTMG: polytetramethylene ether glycol) have also been reported. In our previous study, we demonstrated that the PEF-mb-PTMG with 20 wt% PTMG as soft segment exhibited greatly improved ductility (elongation at break 250%) and retained high tensile strength of 74 MPa at the same time, and the PEF-mb-PTMG with 35 wt% PTMG even manifested supertough nature, with Izod notched impact strength over 50 kJ/m². However, unfortunately, incorporating PTMG into PEF greatly sacrifices the gas barrier properties [30]. The research progress in PEF modification are briefly summarized in Scheme 1.

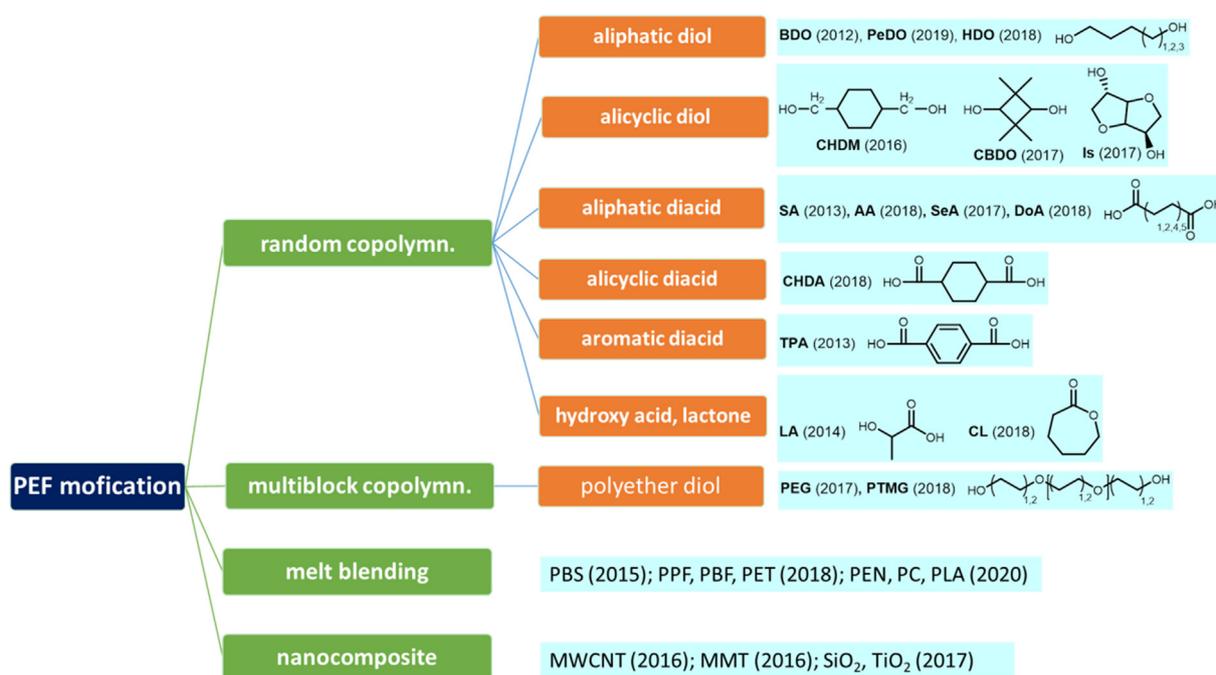
It is well-known that some aliphatic polycarbonates (APCs) such as poly(ethylene carbonate) and poly(propylene carbonate) are characterized by high gas barrier performance [31]. But they are not thermally stable at high temperature. Usually, APC with longer alkylene group in the repeat unit has better thermal stability [32]. Accordingly, APC or its diol with butylene or longer alkylene moiety may be thermally stable to endure the high temperature needed to modify PEF through blending or copolymerization. In fact, some APC diols synthesized from dimethyl carbonate, a well-known “green chemical”, and linear α,ω -alkanediois are widely used in synthesizing poly(carbonate-urethane)s with better hydrolysis resistance, mechanical properties and chain mobility at low temperature than poly(ether-urethane)s [33–35]. As potentially biodegradable polymers, poly(butylene carbonate-co-furandicarboxylate)s [36,37] have been reported to show clearly higher gas barrier properties than the commercially available biodegradable copolyester Ecoflex®. However, to the best of our knowledge, PEF copolymers containing APC moiety has not yet been reported in literature.

As one of the series of studies on PEF modification [19,24,30], a commercially available aliphatic copolycarbonate diol, PPeHC diol, a copolycarbonate diol produced from 1,5-pentylene diol (PeDO), 1,6-hexylene diol (HDO) and dimethyl carbonate, was used as a third component to modify PEF in this work. In brief, PEF-based copolymers were synthesized via melt polycondensation of dimethyl 2,5-furandicarboxylate and ethylene glycol in the presence of PPeHC diol. The chemical structure and thermal properties of the products were characterized with ¹H NMR, ¹³C NMR, DSC and TGA, the mechanical properties were assessed by tensile and notched Izod impact test, and gas barrier performance was evaluated by O_2 and CO_2 permeation testing.

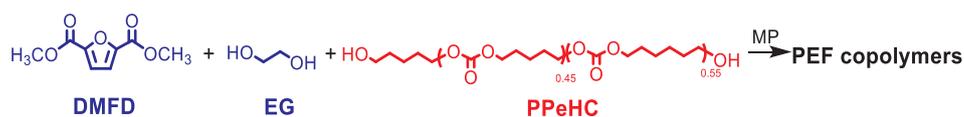
2. Experimental section

2.1. Materials

Dimethyl 2,5-furandicarboxylate (DMFD, 99.3%) and ethylene glycol (EG, 99%) were purchased from Mianyang ChemTarget. Co. Ltd (China) and Sigma-Aldrich respectively. PPeHC, a copolycarbonate diol produced from 1,5-pentylene diol (PeDO), 1,6-hexylene diol (HDO) and



Scheme 1. Brief summary of the research progress in PEF modification. (the number in the parenthesis means the year at which the monomer, polymer or filler was reported for PEF modification for the first time.



Scheme 2. Schematic diagram of synthesis of PEF copolymers.

dimethyl carbonate was purchased from Shenzhen Jason-Material Co. Ltd (China). According to the supplier, the molar percentage of hexylene carbonate repeat unit (ϕ_{HC}) and number-average molecular weight (M_n) are 55 mol% and 2000 g/mol, respectively. Home-made titanium-based catalyst (Ti@Si, Ti 1 wt% or 0.21 mmol Ti/g)¹⁹ and Irganox 1010 (BASF) were used as the catalyst and antioxidant for polymer synthesis, respectively. Deuterated chloroform (CDCl₃), deuterated trifluoroacetic acid (TFA-d₁), phenol and 1,1,2,2-tetrachloroethane (TCE) were all purchased from Sinopharm. All the chemical reagents were used as received.

2.2. Synthesis

The PEF-based copolymers were synthesized by a two-step process, namely, transesterification and polycondensation of DMFD and EG in the presence of PPeHC diol. The molar ratio EG/DMFD was fixed at 2.0. The mass of PPeHC in the feed (m_{PPeHC}) was determined by Eq. (1), where ϕ_{PPeHC} is the designed mass percentage of PPeHC segment that will be incorporated into the copolymers, m_{DMFD} was the mass of DMFD in the feed, 182 and 184 are the molecular weights of ethylene 2,5-furandicarboxylate (EF) repeat unit and DMFD monomer, respectively.

$$\phi_{\text{PPeHC}} (\text{wt}\%) = \frac{m_{\text{PPeHC}}}{m_{\text{PPeHC}} + \frac{182m_{\text{DMFD}}}{184}} \times 100\% \quad (1)$$

In the first step, the predetermined amounts of DMFD, EG, PPeHC-diols, antioxidant (Irganox 1010, 0.25 wt% of the monomers) and catalyst (0.1 wt% of DMFD) were added into a 250 mL four-necked round-bottom reactor equipped with a mechanical stirrer, N₂ inlet and reflux condenser. Then, the reactor was heated stepwise from 170 °C to 200 °C for about 4 h under N₂ atmosphere until no methanol was distilled out. In the second step, the polycondensation reaction was carried out by raising the reaction temperature to 230 °C and reducing the pressure to about 100 Pa. After 1 h, the reaction temperature was raised to 240 °C and the reaction was allowed to conduct until the so-called Weissenberg effect emerged. PEF was synthesized with the same procedure in the absence of PPeHC. Finally, the products were dried at 60 °C in vacuum without any purification. The resulting copolymers are named as PEF- ϕ_{PPeHC} .

2.3. Characterization

Intrinsic viscosity [η] of the (co)polymers was measured by an semi-automatic viscosity tester (ZONWON IVS300, China) equipped with a Ubbelohde viscometer at a concentration of 5 g/dL in a mixture of solvents, i.e., phenol/TCE (3/2, w/w), at 25 °C.

¹H and ¹³C NMR spectra of the (co)polymers were recorded with a Bruker AC-80 (400 M). Deuterated trifluoroacetic acid (TFA-d₁) was used as solvent and tetramethylsilane as internal reference.

Thermal transition of the (co)polymers was measured with differential scanning calorimetry (DSC) on a TA-Q200 (TA Instrument, USA) thermal analyzer using the traditional heating-cooling-heating cycle. The same heating/cooling rate of 10 °C/min and isothermal time of 5 min were applied to all samples. But different temperature ranges were used for the samples: -90–100 °C for PPeHC diol, 30–250 °C for PEF and -90–250 °C for the copolymers.

Thermogravimetric analysis (TGA) of the (co)polymers was conducted with a TA Q500 (TA Instrument, USA). All the samples were heated from 50 to 600 °C at 10 °C/min under nitrogen atmosphere.

Specimens for mechanical test (tensile: dumbbell-shaped, 2 mm in thickness and 4 mm in width; impact: rectangular, 80 × 10 × 4 mm³)

were prepared by a HAAKE MiniJet Injection moulding machine, notched (only for impact test) and then conditioned at room temperature for at least 48 h before testing. Tensile tests were conducted with a Zwick Roell Z020 (Zwick, Germany) testing machine at 25 °C according to ASTM D638. A crosshead speed of 10 mm/min was adopted for all the specimens. Notched Izod impact tests were carried out using a CEAST Resil impact tester (CEAST, Italy) with a pendulum of 5.5 J according to ASTM D256. For each sample, at least five specimens were tested.

Gas barrier properties were measured at 23 °C and relative humidity of 50% by using a BSG-33E gas permeability tester (Labstone Instruments Technology Co., Ltd). O₂ and CO₂ with high purity of 99.9% were used. The film samples were prepared using the similar procedures as our previous reports [24,30]. The gas permeation coefficients of oxygen permeation standard films made of PET (thickness 23 μm, permeance of 69.427 ± 10% cm³/(m².d.0.1 atm), provided by Labstone Co. Ltd.) were also measured under the same condition for comparison.

3. Results and discussion

3.1. Synthesis and structure characterization

PEF and a series of PEF copolymers were synthesized through the two-step process in the presence of PPeHC diols, as shown in Scheme 2. The synthetic conditions and results are listed in Table 1. The copolymers with Intrinsic viscosity (IV) as high as 0.80–1.11 dL/g were achieved within relatively short polycondensation time (2.5–3 h). Furthermore, the presence of PPeHC diol seemed to promote the polycondensation reaction and as a result, higher intrinsic viscosity was achieved at shorter reaction time with increasing PPeHC content. Similar results were also observed in the synthesis of PEF-mb-PTMG in our previous study [30].

The ¹H NMR spectra of the PEF copolymers are shown in Fig. 1, together with those of PEF and PPeHC diol. For the PPeHC diol, the outer and middle methylene protons in PeC and HC units show the same chemical shifts at 4.38 ppm (d) and 1.88 ppm (e), respectively, but the inner methylene protons in PeC and HC units appear separately at 1.63 ppm (f) and 1.58 ppm (g). Besides, the resonance signal appearing at 4.58 ppm (h) corresponds to the CH₂ neighboring terminal hydroxyl group. According to the chemical shift attribution, the

Table 1
Synthetic conditions^a and structural characterization of PEF copolymers.

Run	ϕ_{PPeHC} ^b (wt %)	t_{mp} ^c (h)	IV ^d (dL/g)	ϕ_{EF} ^e (mol%)	ϕ_{RC} ^f (mol%)	ϕ_{RF} ^g (mol%)	ϕ_{EC} ^h (mol%)
1	0	3	0.81	100	0	0	0
2	10	2	0.80	85.7	11.3	1.5	1.5
3	15	2	0.83	75.5	13.5	5.5	5.5
4	20	1.5	0.84	67.2	16.8	8.0	8.0
5	25	1.5	0.96	58.3	19.5	11.1	11.1
6	30	1.5	0.89	48.8	21.2	15.0	15.0
7	35	1.5	1.11	38.0	21.2	20.4	20.4
8	40	1.5	0.91	26.4	20.2	26.7	26.7

^aTransesterification: catalyst 0.1 wt% of DMFD, EG/DMFD molar ratio 2.0, 170–200 °C/4h; Polycondensation: 230 °C/1h + 240 °C/ t_{mp} . ^bDesigned mass percentage of PPeHC in copolymers, calculated with Eq. (1). ^cMelt polycondensation time at 240 °C. ^dIntrinsic viscosity, phenol/TCE (3/2, w/w), 25 °C. ^{e–h}Molar percentage of EF, RF (=PeF + HF), EC and RC (=PeC + HC) units in the copolymers, ignoring the presence of DEGF and DEGC units.

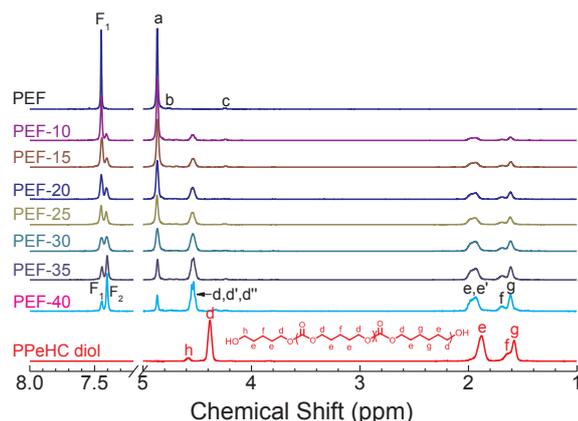


Fig. 1. ^1H NMR spectra of PPeHC, PEF and PEF copolymers (TFA- d_1 as solvent).

composition (ϕ_{HC}) of PPeHC diol, the average molecular weight of the repeat units (M_{RC} , $R = \text{Pe}$ and H) and the number-average molecular weight (M_{n}) of the PPeHC diol were calculated from Eqs. (2)–(4), respectively, in which I_x is the peak area of the chemical shift x ($x = \text{d}, \text{f}, \text{g}, \text{h}$), 104, 118, 130 and 144 are the molecular weights of 1,5-pentanediol, 1,6-hexanediol, pentylene carbonate unit (PeC) and hexylene carbonate unit (HC), respectively. The calculated ϕ_{HC} and M_{n} values are 54.5 mol% and 1810 g/mol, agreeing well with the values (55 mol%, 2000 g/mol) provided by the supplier. The average molecular weight of the repeating units is 137.6 g/mol.

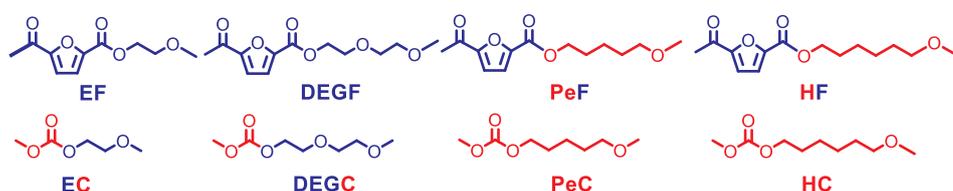
$$\phi_{\text{HC}}(\text{mol}\%) = \frac{I_{\text{g}}}{2I_{\text{f}} + I_{\text{g}}} \times 100\% \quad (2)$$

$$M = 130 \times (1 - \phi_{\text{HC}}) + 144 \times \phi_{\text{HC}} \quad (3)$$

$$M_{\text{n}} = \frac{I_{\text{d}}}{I_{\text{h}}} \times M + 104 \times (1 - \phi_{\text{HC}}) + 118 \times \phi_{\text{HC}} \quad (4)$$

For PEF, the signals at 7.44 ppm (F_1), 4.86 ppm (a), 4.74 ppm (b) and 4.23 ppm (c) are attributed to the following protons: CH in furan ring unit, CH_2 in EG unit, the outer and inner CH_2 in diethylene glycol furandicarboxylate (DEGF) unit, respectively. The DEGF unit was formed by etherification side reaction during the polycondensation [38].

For the copolymers, the signals from both PEF and PPeHC appear, and the later move to lower field. But the signal of CH in furan ring splits into two peaks at 7.44 ppm (F_1) and 7.40 ppm (F_2). Furthermore, the peak areas of F_2 and d are clearly larger than the values expected for segmented or multiblock copolymers. These results suggest that ester-carbonate exchange reactions occurred during melt polycondensation and as a result, some new repeat units (PeF, HF, EC, DEGC) besides EF, DEGF, PeC and HC were formed in the resulting random copolymers, as shown in Scheme 3. The attribution of the chemical shifts of various structure units in the copolymers are shown in Scheme 4. In brief, the signals F_1 and F_2 are attributed to the CH in furan ring connected to ethylene/DEG and pentylene/hexylene, respectively. The chemical shifts of the CH_2 groups neighbouring the carbonate bonds in PeC and HC (d) and neighbouring the ester bonds in PeF and HF (d') and neighbouring the carbonate bonds in EC (d'') overlap at 4.5–4.6 ppm. Similarly, the chemical shifts of the CH_2



Scheme 3. The repeat units in the “randomized” copolymers as a result of ester-carbonate exchange reactions occurring along melt polycondensation.

groups neighbouring the d and d' CH_2 groups in PeC/HC (e) and PeF/HF (e') overlap at 1.9–2.0 ppm. The content of DEGC units is very low so that the chemical shifts of the CH_2 groups in DEGC (c' , d'') are unidentifiable.

The random structure of the copolymers was further validated by the ^{13}C NMR spectra shown in Fig. 2. The chemical shift attribution is also shown in this figure. Clearly, the signals of the C atoms in the furandicarboxylate ester carbonyl groups are splitted into four peaks (S_1, S_2, S_3, S_4) at 146–147.2 ppm. They are attributed to the chemical shifts of EFE, EFR ($R = \text{Pe}$ or H) and RFR triads, respectively. From the above structure characterization, it can be concluded that random copolymers rather than block ones were formed via ester-carbonate exchange reactions during melt polycondensation.

Based on the chemical shift attribution in the ^1H NMR spectra, the copolymer composition, namely, the molar percentages ($\phi_{\text{EF}}, \phi_{\text{RF}}, \phi_{\text{EC}}, \phi_{\text{RC}}$) of EF, RF (PeF + HF), EC and RC (PeC + HC) units, can be calculated from Eqs. (5)–(9), considering that the amount of DEGF and DEGC units is so low that it can be ignored. The results are listed in Table 1. As the EC unit is relatively unstable at the melt polycondensation temperature, the true values of the molar percentage of EC unit may be lower than the calculated ones. Besides, the molar percentage of hexylene in the sum of pentylene and hexylene in the copolymers (55.2 ± 0.9 mol%, also calculated from Eq. (2)) kept unchanged as compared with the ϕ_{HC} value (54.5 mol%) in the starting material, PPeHC diol.

$$\phi_{\text{RC}} = \frac{\varphi_{\text{PPeHC,w}}/137.6}{\varphi_{\text{PPeHC,w}}/137.6 + (1 - \varphi_{\text{PPeHC,w}})/182} \quad (5)$$

$$\phi_{\text{EF}} = \frac{I_{\text{a}}}{I_{\text{d}} + \text{d}' + \text{d}'' + I_{\text{a}}} \times 100\% \quad (6)$$

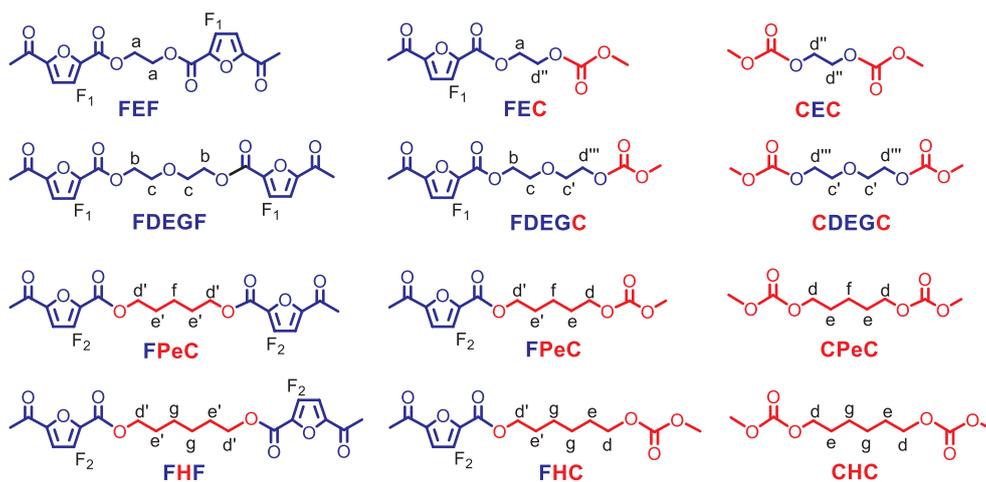
$$\phi_{\text{RC}} + \phi_{\text{RF}} + \phi_{\text{EC}} = 1 - \phi_{\text{EF}} \quad (7)$$

$$\phi_{\text{RC}} = \phi_{\text{RC}} - (\phi_{\text{EF}} - \phi_{\text{EF}}) = \phi_{\text{RC}} - ((1 - \phi_{\text{RC}}) - \phi_{\text{EF}}) \quad (8)$$

$$\phi_{\text{RF}} = \phi_{\text{EC}} = (1 - \phi_{\text{RC}} - \phi_{\text{EF}})/2 \quad (9)$$

3.2. Thermal transition behavior

The DSC thermograms of PEF, PPeHC diol and the copolymers are displayed in Figs. S1. As PEF is characterized by weak crystallizability [11,30,38] ascribed to its restricted chain mobility [39], only weak melting peaks appeared in the 1st and 2nd heating scans (ΔH_{m} 10.7 J/g and 1.2 J/g at about 213 °C, respectively), but no melt crystallization peak was observed during the cooling scan. The PEF sample showed a high T_{g} (89 °C) due to its restricted chain mobility and high intrinsic viscosity. The PPeHC diol showed neither crystallization peak nor melting peak in all three DSC scans, illustrating its completely amorphous feature. Although both poly(pentylene carbonate) and poly(hexylene carbonate) diols are crystallizable [40], random PPeHC copolymer diol with ϕ_{HC} of 50–60 mol% and M_{n} of about 2500 g/mol are reported to be amorphous viscous liquid with glass transition temperature (T_{g}) from -54 °C to -50 °C [41]. In this study, the PPeHC diol showed a T_{g} value of -52 °C, agreeing well with literature data [41]. The PEF copolymers are all amorphous. Only a single T_{g} was observed for all copolymers in the DSC thermograms. As shown in Fig. 3, it is found that the T_{g} of the copolymers decreases almost linearly with



Scheme 4. Attribution of the chemical shifts of various structure units.

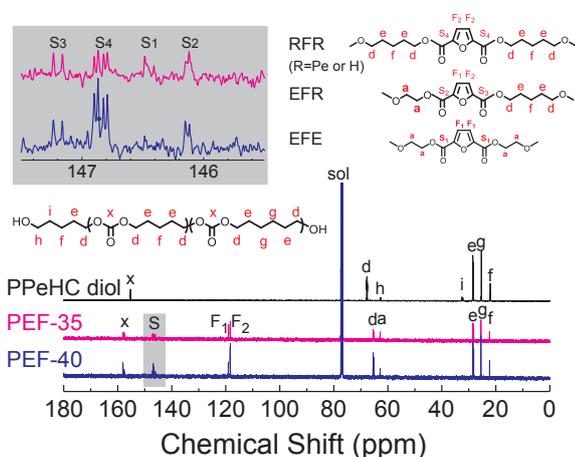


Fig. 2. ^{13}C NMR spectra of PPeHC diol and two PEF-based copolymers.

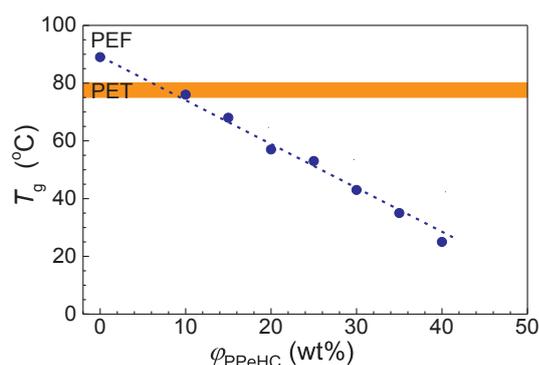


Fig. 3. Linear decrease of glass transition temperature (T_g) of the copolymers with the PPeHC diol feeding ratio, φ_{PPeHC} .

increasing φ_{PPeHC} . The T_g value decreases by 1.6 °C by introducing 1 wt % PPeHC diol within the copolymer. Consequently, the copolymers in this study have T_g lower than PET (75–80 °C) though PEF has T_g (89 °C) higher than PET.

3.3. Thermal stability

Thermal stability of the PEF and PEF copolymers was investigated by TGA under N_2 atmosphere. The TGA and DTG curves are shown in Fig. 4, and their decomposition temperatures at 5% weight loss ($T_{d,5}$)

and maximum decomposition rate ($T_{d,\text{max}}$) and residual mass percentage at 600 °C (R_{600}) are listed in Table S1. The PEF sample showed $T_{d,5}$ of 376 °C, $T_{d,\text{max}}$ of 416 °C and R_{600} of 14.8%. Both the $T_{d,5}$ and $T_{d,\text{max}}$ of PEF are lower than those of PET (407 °C, 440 °C [18]). In comparison with PEF, the copolymers did show earlier weight loss and clearly lower $T_{d,5}$ and $T_{d,\text{max}}$. The copolymers exhibited $T_{d,5}$ of 351–339 °C, $T_{d,\text{max}}$ of 399–379 °C and R_{600} of 10.9%–4.2%, which decreased with the increasing φ_{PPeHC} from 10 wt% to 40 wt%. These results indicate that the presence of the carbonate units in the copolymers results in some reduction of thermal stability, which can be readily explained by the thermally induced degradation of carbonate groups via unzipping, β -H transfer and decarboxylation reactions at high temperature [42].

3.4. Mechanical properties

The typical tensile curves of PEF and the copolymers are shown in Fig. 5(A). The Young's modulus (E), tensile strength at yield (σ_y) and break (σ_b), and elongation at yield (ϵ_y) and break (ϵ_b) are summarized in Table 2. The composition dependence of tensile properties are plotted in Fig. 5B–D. As expected from the high intrinsic viscosity and chain rigidity, the PEF sample displayed brittle tensile behavior. In comparison with bottle-grade PET [24,43], PEF showed higher Young's modulus (3.4 GPa vs 2.4–1.9 GPa) and tensile strength at maximum (84 MPa vs 67–58 MPa) but much lower elongation at break (3% vs 20–324%). The copolymers PEF-10 and PEF-20 still behaved as brittle materials like PEF, showing unchanged elongation at break (ϵ_b 3–4%) and slightly decreased rigidity (E 3.1–2.7 GPa) and strength (σ_b 81–72 MPa).

Interestingly enough PEF-25 and PEF-30 showed clear yielding/necking and greatly improved ductility (elongation at break 21–194%), indicating that brittle-ductility transition occurred at φ_{PPeHC} between 20 wt% and 25 wt%. These two copolymers still retained high Young's modulus (2.2–1.9 GPa vs 2.4–1.9 GPa) and yield/maximum strength (69–58 MPa vs 67–58 MPa) comparable to bottle-grade PET [24,43] though the breaking strength was relatively low. No obvious necking was observed for PEF-35, but weak yielding still appears in the tensile curve. The elongation at break increased to 275%, but the Young's modulus drastically decreased to 0.91 GPa and the yield strength decreased to 23 MPa. Differently, PEF-40 manifested tensile feature of typical elastic polymer as its T_g is close to room temperature. It has a low Young's modulus (10 MPa). Its elongation at break (203%) is lower than that of PEF-35 possibly because of its lower intrinsic viscosity (0.91 vs. 1.11 dL/g). But as a thermoplastic elastomer, its breaking strength is very high (23 MPa). Therefore, this copolymer appears to be a high performance elastomer.

The notched Izod impact strength (σ_i) of the copolymers was also

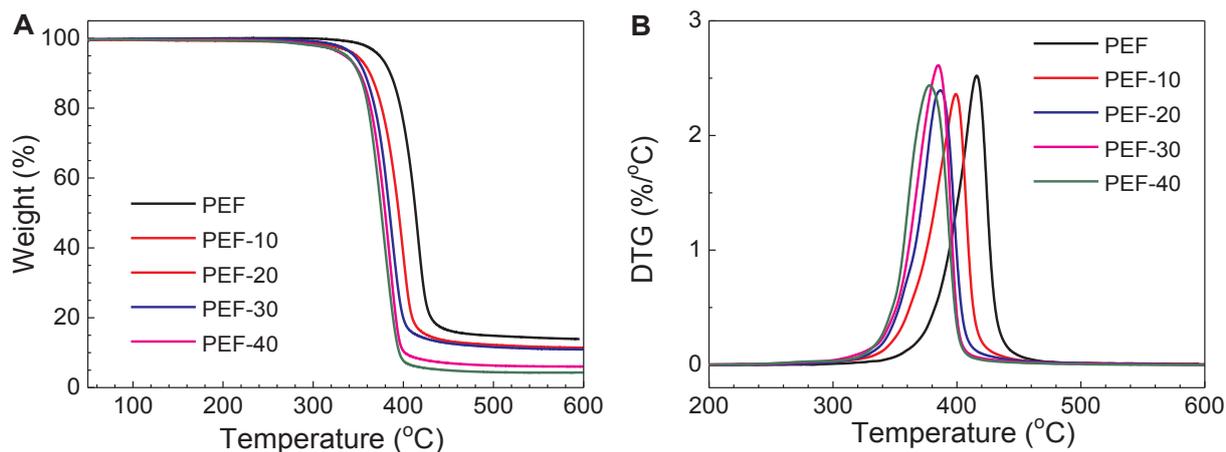


Fig. 4. TGA (A) and DTG (B) thermograms of PEF and the copolymers. (N_2 atmosphere, $10\text{ }^\circ\text{C}/\text{min}$).

measured, and the results are listed in Table 2. Although the ductility was greatly improved at ϕ_{PPEHC} of 25–30 wt%, the impact strength was only slightly improved to 2.3–2.5 kJ/m^2 until the ϕ_{PPEHC} reaches 30–35 wt%, which is still lower than PET (2.7 kJ/m^2) [24]. In contrast, the PEF-40 specimens were not ruptured in the impact test due to elastomer feature. The brittle-toughness transition occurred only at very high ϕ_{PPEHC} (35–40 wt%). It can be concluded that PPEHC diol is less efficient than PTMG diol in toughening PEF via copolymerization. This can be explained by the random nature of the PPEHC-based copolymers (*vide supra*) in this work instead of the multiblock nature of the PTMG-based copolymers in our previous work [30].

3.5. Gas barrier properties

Finally, the O_2 and CO_2 barrier properties of PEF-25, PEF-30 and PEF-40 were measured and compared with those of PEF as well as PET standard film (see Table 3). The gas barrier improvement factor (BIF) was defined as the gas permeability coefficient (P) of PET divided by the permeability coefficient of the target polymer. Higher BIF stands for better gas barrier properties.

As reported by Burgess, the hindrance of furan ring flipping is responsible for the high gas barrier performance of PEF [39]. In this study, the PEF sample also exhibited much better gas barrier properties than PET, with BIF_{O_2} of 2.0 and BIF_{CO_2} of 10. Because CO_2 is more

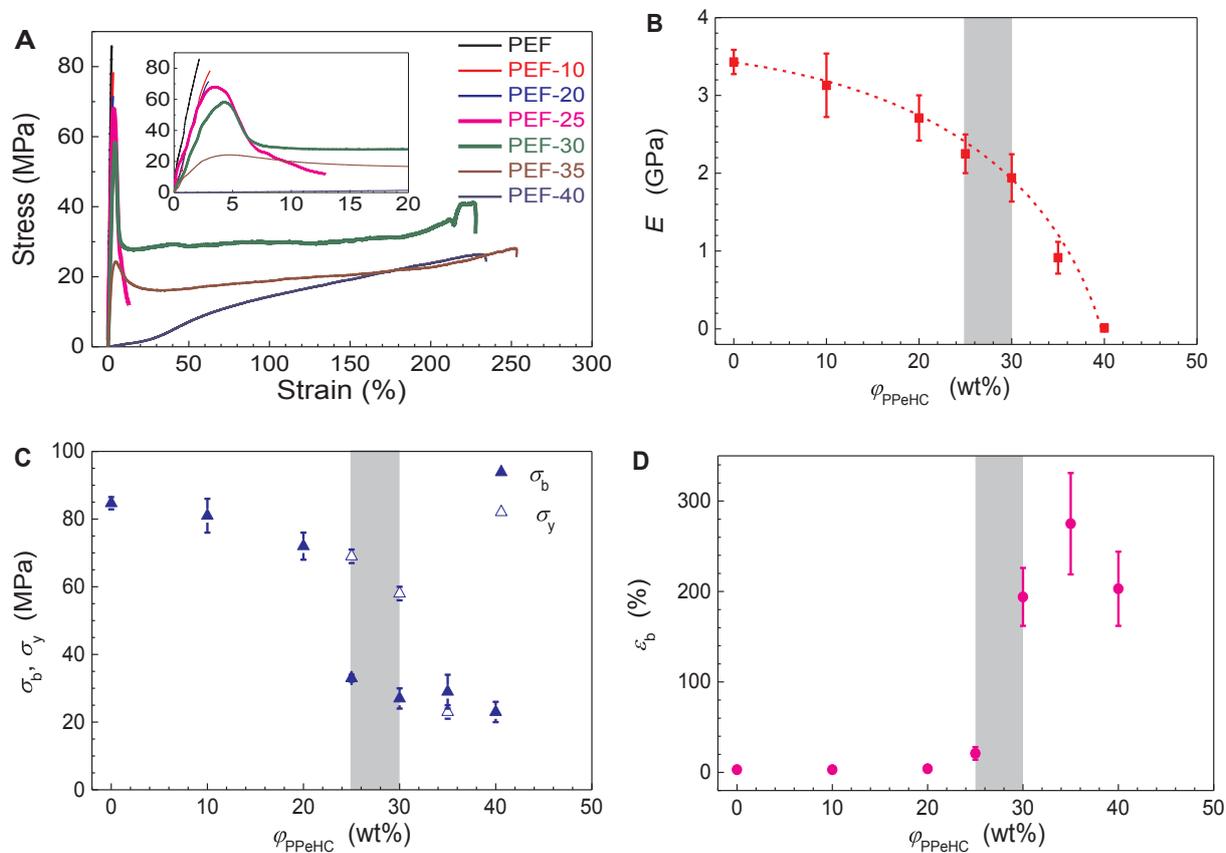


Fig. 5. Typical stress-strain curves of PEF and PEF copolymers (A) and composition dependences of the Young's modulus (B), tensile strength (C), elongation at break (D) of PEF and PEF copolymers.

Table 2Young's modulus (E), tensile strength at yield (σ_y) and break (σ_b), elongation at yield (ϵ_y) and break (ϵ_b), and notched impact strength (σ_i) of PEF and PEF copolymers.

Sample	E (GPa)	σ_y (MPa)	σ_b (MPa)	ϵ_y (%)	ϵ_b (%)	σ_i (kJ/m ²)
PEF	3.43 ± 0.16	–	84 ± 2	–	3 ± 1	2.1 ± 0.1
PEF-10	3.13 ± 0.41	–	81 ± 5	–	3 ± 1	2.1 ± 0.1
PEF-20	2.71 ± 0.29	–	72 ± 4	–	4 ± 1	2.1 ± 0.3
PEF-25	2.25 ± 0.25	69 ± 2	30 ± 4	3 ± 1	21 ± 7	2.1 ± 0.2
PEF-30	1.94 ± 0.30	58 ± 2	27 ± 3	4 ± 1	194 ± 32	2.3 ± 0.2
PEF-35	0.914 ± 0.20	23 ± 2	29 ± 5	5 ± 1	275 ± 56	2.5 ± 0.3
PEF-40	0.01 ± 0.002	–	23 ± 3	–	203 ± 41	not broken
PET [24]	1.93 ± 0.06	67 ± 3	39 ± 2	3.8 ± 0.2	324 ± 4	2.7 ± 0.3
PET [43]	2.41 ± 0.19	58 ± 0.2	–	–	20 ± 1.6	–

Table 3O₂ and CO₂ barrier properties of PET, PEF and PEF-based copolymers.

Sample	T (°C)	$P_{O_2}^a$ (barrer)	$BIF_{O_2}^b$	$P_{CO_2}^a$ (barrer)	$BIF_{CO_2}^b$	Ref.
PET ^c	23	0.022	1	0.12	1	This work
PEF	23	0.011	2.0	0.012	10	This work
PEF-25	23	0.027	0.81	0.033	3.6	This work
PEF-30	23	0.032	0.69	0.042	2.8	This work
PEF-40	23	0.053	0.42	0.20	0.60	This work
PEF-mb-PTMG20	23	0.051	0.43	0.11	1.1	[30]
PEF-mb-PTMG40	23	0.28	0.079	1.2	0.1	[30]

^aMeasured oxygen or carbon dioxide permeability coefficient of polymers in the unit "barrer": 1 barrer = $7.50 \times 10^{-18} \text{ m}^2 \cdot \text{s}^{-1} \cdot \text{Pa}^{-1}$ or $10^{-10} \text{ cm}^3 \cdot \text{cm} \cdot \text{cm}^{-2} \cdot \text{s}^{-1} \cdot \text{cmHg}^{-1}$. ^bBIF means barrier improvement factor, $BIF_{O_2} = P_{O_2, \text{PET}}/P_{O_2, \text{sample}}$, $BIF_{CO_2} = P_{CO_2, \text{PET}}/P_{CO_2, \text{sample}}$. ^cOxygen permeation standard film made of PET with thickness 23 μm and permeance of $69.427 \pm 10\% \text{ cm}^3/(\text{m}^2 \cdot \text{d} \cdot 0.1 \text{ atm})$.

affiliative than O₂ to the polar carbonyl moieties in PEF, the diffusion coefficient of CO₂ in PEF is lower and therefore the improvement in CO₂ barrier surpasses that in O₂ barrier. Similar trend was also reported by Wang et al. [11] and Burgess et al. [10,12].

Both O₂ and CO₂ barrier properties of the copolymers decrease with increasing φ_{PpEHc} . At φ_{PpEHc} of 25 and 30%, the BIF_{O_2} value decreases to 0.81 and 0.69. In other words, these two copolymers are inferior to PET in O₂ barrier performance. However, they still superior to PET in CO₂ barrier performance, as evidenced by their BIF_{CO_2} values of 3.6 and 2.8 respectively. PEF-40 is not as good as PET in O₂ and CO₂ barrier performance as its BIF_{O_2} (0.42) and BIF_{CO_2} (0.60) values are less than 1.0. But as a thermoplastic elastomer, it has much higher gas barrier performance than the classical gas-tight rubber, namely, butyl rubber (P_{O_2} 1.28 barrer) [44]. When compared with PEF-mb-PTMG [30], it is obvious that these PEF copolymers exhibit much better O₂ and CO₂ barrier performance. Therefore, as a comonomer for PEF modification via copolymerization, PpEHc diol is better than PTMG diol in keeping PEF's gas barrier properties though it is inferior in improving the ductility and impact toughness.

4. Conclusions

A series of PEF-based copolymers with high intrinsic viscosity were synthesized via melt polycondensation of ethylene glycol and dimethyl 2,5-furandicarboxylate in the presence of 10–40 wt% copolycarbonate diol, PpEHc diol. Because of ester-carbonate exchange reactions occurring during melt polycondensation, they are all randomized and amorphous copolymers, possessing composition-dependent physical and mechanical properties tunable from rigid-to-ductile thermoplastics to thermoplastic elastomers. Among them, PEF-25 and PEF-30 are thermoplastics possessing improved ductility (elongation at break 21%–194%) and retaining high tensile modulus (2.2–1.9 GPa) and yielding strength (69–58 MPa) comparable to PET as well as CO₂ barrier performance higher than PET (BIF_{CO_2} 3.6–2.8). In contrast, PEF-40 is a high performance thermoplastic elastomer with high tensile strength (23 MPa) and excellent gas barrier performance far exceeding typical gas-tight butyl rubber.

Data availability

The raw/processed data required to reproduce these findings cannot be shared at this time due to technical or time limitations. Data will be made available upon request.

CRediT authorship contribution statement

Hongzhou Xie: Conceptualization, Methodology, Investigation, Validation, Writing - original draft. **Linbo Wu:** Conceptualization, Writing - review & editing, Visualization, Supervision, Project administration, Funding acquisition. **Bo-Geng Li:** Supervision. **Philippe Dubois:** Supervision, Writing - review & editing.

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.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.eurpolymj.2020.109856>.

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