



# Aliphatic polycarbonate modified poly(ethylene furandicarboxylate) materials with improved ductility, toughness and high CO<sub>2</sub> barrier performance

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## ABSTRACT

Poly(ethylene 2,5-furandicarboxylate) (PEF) is a promising biobased polymer possessing high strength, rigidity and gas barrier performance, but its poor ductility and toughness may limit its practical applications. In order to obtain PEF materials with improved ductility and impact toughness as well as high strength, modulus and excellent gas barrier performance, PEF with relatively low molecular weight was modified with aliphatic polycarbonate (APC) diols by chain extension/coupling in this study. The resulting products were mixtures composed of randomly segmented copolymers, chain extended APC and chain extended PEF. The APC moiety was proved to be partially miscible with the PEF matrix, and therefore plasticized the PEF matrix and promoted its cold crystallization. In comparison with PEF, the modified PEFs possess significantly enhanced tensile ductility and impact toughness. Particularly, the modified PEF containing 15 wt% poly(hexamethylene carbonate) exhibits balanced mechanical properties and CO<sub>2</sub> barrier 5 times to PET.

## 1. Introduction

As a biobased counterpart of the most widely used poly(ethylene terephthalate) (PET) polyester, poly(ethylene 2,5-furandicarboxylate) (PEF) synthesized from ethylene glycol and biobased 2,5-furandicarboxylic acid or its diester possesses not only huge resource and environmental benefits [1] but also better thermal and mechanical performances [2] and superior gas barrier properties than PET [3,4]. It has been widely reported that PEF has several times to one magnitude order improvement in O<sub>2</sub> and CO<sub>2</sub> barrier performance when compared with PET [3,4]. These high performances endow PEF with great competitiveness for eco-packaging application in O<sub>2</sub> and CO<sub>2</sub> sensitive foods and beverages demanding high gas barrier performance and high mechanical properties. However, PEF exhibits poor tensile ductility (elongation at break 1–5%) [5,6] without being biaxial-orientated [7] and also poor impact toughness (3.1 kg cm/cm [8]). Clearly, such

shortcomings will limit its applications.

In order to modify PEF, copolymerization [8–20] and blending [21–23] have been extensively reported in recent years. For PEF modification, it is very desirable that both ductility and impact toughness can be greatly improved simultaneously by adding as little modifiers as possible and at the same time, its inherent high tensile strength and modulus, gas barrier performance and glass transition temperature can be maintained as much as possible. However, this is still a very challenging work. For an example, PEF/PBS blends showed satisfactory impact strength as high as 15.5 kJ/m<sup>2</sup> [21], but its ductility is still poor. For PEF modification by random copolymerization, diols [8–14] seem to be better choice than diacids [15–17] and lactones [18] in maintaining strength/modulus and gas barrier properties as well as improving ductility. In one of our previous studies [13], it was found that the ductility of poly(ethylene-co-pentylene 2,5-furandicarboxylate) (PEPeF) random copolyester was greatly improved by incorporating only 18 mol

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% PEF unit, and the copolymer maintained PEF-comparable tensile modulus (3.3 GPa) and yielding strength (83 MPa), PET-comparable  $T_g$  (75 °C) and high O<sub>2</sub> and CO<sub>2</sub> barrier property (4.8 and 8.6 times to PET). But random PEF copolymers, whether the comonomers are diacids, diols or lactones, often manifest low impact toughness [12–14], unless very large amount of comonomer is introduced into the copolymers [8].

In comparison with random copolymerization, block copolymerization is more effective to improve tensile ductility and impact toughness simultaneously. In our previous study [20], we demonstrated that PEF-*mb*-PTMG multiblock copolymers containing  $\geq 30$  wt% poly(tetramethylene glycol) (PTMG) as soft segment exhibited excellent ductility and impact toughness. But the tensile strength and O<sub>2</sub> barrier property were significantly weakened at the same time.

Aliphatic polycarbonates (APCs) are flexible polymers with low glass transition temperature and often used as soft segments in poly(carbonate-urethane)s which display better hydrolysis resistance and mechanical properties at low temperature than conventional poly(ester-urethane)s [24–26]. It is also well-known that some APCs like poly(ethylene carbonate) and poly(propylene carbonate) have high gas barrier performance [27]. Poly(butylene carbonate-co-furandicarboxylate) (PBCF), a potentially biodegradable poly(carbonate-co-ester) reported by Cai et al. [28] and Hu et al. [29] manifested clearly higher gas barrier properties [29] than poly(butylene adipate-co-terephthalate) (PBAT), a well-known biodegradable copolyester. In our previous study [14], poly(pentylene-co-hexylene carbonate) (PPeHC) diol, a commercial APC diol, was used to modify PEF and randomized PEF-*r*-PPeHC copolymers were synthesized. The copolymers exhibited much better O<sub>2</sub> and CO<sub>2</sub> barrier performance [14] when compared with PEF-*mb*-PTMG [20]. But the impact toughness was still far from expectation.

In this study, APC modified PEF materials were prepared via chain extension/coupling of PEF and APC diols with hexamethylene diisocyanate as chain extender/coupler to avoid randomization. The chemical structure, thermal, mechanical and gas barrier properties of the products were characterized and measured. In comparison with the PEF-*r*-PPeHC copolymers [14], these materials display comparable gas barrier properties but superior impact toughness.

## 2. Experimental section

### 2.1. Materials

2,5-Furandicarboxylic acid (FDCA, 99%), ethylene glycol (EG, 99%) and tetrabutyl titanate (TBT) were purchased from Jiaying Ruiyuan Biotech Co. Ltd., Sigma-Aldrich and TCI chemicals Co. Ltd., respectively. 1,6-Hexylene diol (HDO), dimethyl carbonate (DMC) and hexamethylene diisocyanate (HDI) were all purchased from Aladdin Reagent Co. Anhydrous potassium carbonate, deuterated chloroform (CDCl<sub>3</sub>), deuterated trifluoroacetic acid (d<sub>1</sub>-TFA), phenol and 1,1,2,2-tetrachloroethane (TCE) were all purchased from Sinopharm Chemical Reagent Co. Ltd. All the chemical reagents were used as received. PPeHC, a polycarbonate diol produced from 1,5-pentanediol (PeDO), HDO and DMC, was purchased from Shenzhen Jason-Material Co. Ltd., China. It appears a viscous liquid. According to the supplier, the molar percentage of hexylene carbonate repeat unit ( $\varphi_{HC}$ ) and number-average molecular weight ( $M_n$ ) are of 55 mol% and 2000 g/mol, respectively. From our <sup>1</sup>H NMR result, the  $\varphi_{HC}$  and  $M_n$  values were calculated to be 54.5 mol% and 1810 g/mol, respectively. The intrinsic viscosity was measured to be 0.09 dL/g.

### 2.2. Synthesis

**Synthesis of PEF** PEF samples were synthesized from EG and FDCA (2/1 M ratio) via two-step melt polycondensation process in a 500 mL four-necked flask equipped with a mechanical stirrer, nitrogen inlet and reflux condenser. The process was the same as the one reported previously<sup>12–13</sup>. The melt polycondensation stage lasted for 2 or 3 h to obtain

PEF samples with different intrinsic viscosity (IV, 0.50 and 0.82 dL/g). The PEF with lower IV was used for modification and the PEF with higher IV was used for performance comparison.

**Synthesis of PHC diol** Poly(hexamethylene carbonate) (PHC) diol was synthesized from DMC and HDO according to a previously reported two-step melt polycondensation process [30,31] at diol/DMC molar ratio of 1.2/1. The monomers were added into a 500 mL four-necked round-bottom flask equipped with a mechanical stirrer, nitrogen inlet and reflux condenser and heated to 100 °C under N<sub>2</sub> atmosphere, then 0.2 wt% K<sub>2</sub>CO<sub>3</sub> (based on all the monomers) was added as catalyst to start the transesterification reaction. The reaction temperature was gradually raised to 180 °C in 6–7 h. After most of the methanol produced as side product and unreacted DMC were distilled out of the reactor, 0.1 wt% TBT was added and the pressure was reduced to about 100 Pa in 15 min and the temperature was raised to 190 °C to start the melt polycondensation reaction. After 6 h, the reaction was stopped by cooling down the reaction medium. The white solid product was used for characterization without purification. Its intrinsic viscosity was measured to be 0.13 dL/g.

**Preparation of APC-modified PEF materials** The PEF (IV 0.50 dL/g) and an APC diol were added with a predetermined mass ratio into a 100 mL round-bottom flask equipped with a mechanical stirrer and nitrogen inlet. The prepolymers were melted and mixed to each other at 230 °C and then HDI was added with 1.1/1 NCO/OH molar ratio to start the chain extension/coupling reaction. The reaction lasted for about 15 min. For simplicity, the product prepared with  $\gamma$  wt% APC diol in the sum of PEF and APC, was named as PEF-APC <sub>$\gamma$</sub> .

### 2.3. Characterization and testing

Intrinsic viscosity (IV) of the copolymers 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 phenol/TCE (3/2, w/w) mixture solvent, at 25 °C.

<sup>1</sup>H NMR spectra were recorded with a Bruker AC-80 (400 MHz) spectrometer. Deuterated chloroform (CDCl<sub>3</sub>) was used as solvents for the APC prepolymers and trifluoroacetic acid (d<sub>1</sub>-TFA) for PEF and APC-modified PEF materials. Tetramethylsilane was used as internal reference.

Thermal transition was measured with a TA-Q200 (TA Instrument, USA) DSC analyzer, using the traditional heating-cooling-heating mode. The same heating/cooling rate of 10 °C/min and isothermal time of 5 min were applied to all samples.

Thermogravimetric analysis (TGA) of the materials 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.

Tensile testing was conducted with a Zwick Roell Z020 (Zwick, Germany) testing machine at room temperature (25 °C) according to ASTM D638. A crosshead speed of 10 mm/min was used for all the specimens. Notched izod impact testing was carried out using a CEAST Resil impact tester (CEAST, Italy) with a pendulum of 5.5 J according to ASTM D256. For each sample, five specimens were tested. The specimens were prepared by a HAAKE MiniJet Injection moulding machine and then conditioned at room temperature for at least 48 h before testing. The impact specimens were notched before conditioning. The shape and size of specimens were as follows: dumbbell-shaped, 2 mm in thickness and 4 mm in width for tensile testing; rectangular, 80 × 10 × 4 mm<sup>3</sup> for impact testing.

Morphology of the impact fracture surface was observed with SU-3500 (HITACHI, Japan) scanning electron microscopy at an acceleration voltage of 30 kV after thin golden layer coating treatment.

Oxygen and carbon dioxide permeability coefficients were measured at 23 °C using a BSG-33E gas permeability tester (Labstone Instruments Technology Co., Ltd). O<sub>2</sub> and CO<sub>2</sub> with high purity of 99.9% were used as test gases. The film specimens of APC-modified PEFs were prepared by thermal press at 220 °C. The thickness of the films was measured with



**Table 1**  
Synthetic conditions and results of APC-modified PEFs.

	$\phi_{\text{APC}}^{\text{a}}$ (wt%)	$[\eta]^{\text{b}}$ (dL/g)	$\phi_{\text{APC}}^{\text{c}}$ (wt%)	$\phi_{\text{DEGF}}^{\text{d}}$ (mol%)	$\phi_{\text{HC}}^{\text{e}}$ (%)
PEF	0	0.50	0	5.3	–
PEF-PPeHC <sub>15</sub>	15	0.73	16.1	5.2	52.3
PEF-PPeHC <sub>30</sub>	30	1.05	28.8	4.7	53.2
PEF-PPeHC <sub>40</sub>	40	1.67	42.1	5.7	55.8
PEF-PHC <sub>15</sub>	15	0.83	15.3	5.5	100
PEF-PHC <sub>30</sub>	30	0.81	29.6	4.7	100

<sup>a</sup> The mass percentage of APC diol in the sum of APC diol and PEF feeds.

<sup>b</sup> Intrinsic viscosity measured at 25 °C in phenol/TCE (3:2 w/w) solvent mixture.

<sup>c</sup> Mass percentage of APC in the APC-modified PEF calculated from equation (5).

<sup>d</sup> Molar percentage of DEGF unit in the pristine PEF and APC-modified PEFs, calculated with  $\phi_{\text{DEGF}} = I_{\text{c}} / (I_{\text{a}} + I_{\text{c}}) \times 100\%$  from the <sup>1</sup>H NMR results.

<sup>e</sup> Molar percentage of HC unit in the PPeHC segment, calculated with equation (4).

$$M_{\text{n,APC}} = M_{\text{RDO}} + M_{\text{RC}} \times I_{\text{d}} / I_{\text{r}} \quad (1)$$

$$M_{\text{diol}} \text{ (for PPeHC)} = M_{\text{PeDO}} (1 - \phi_{\text{HC}}) + M_{\text{HDO}} \times \phi_{\text{HC}} \quad (2)$$

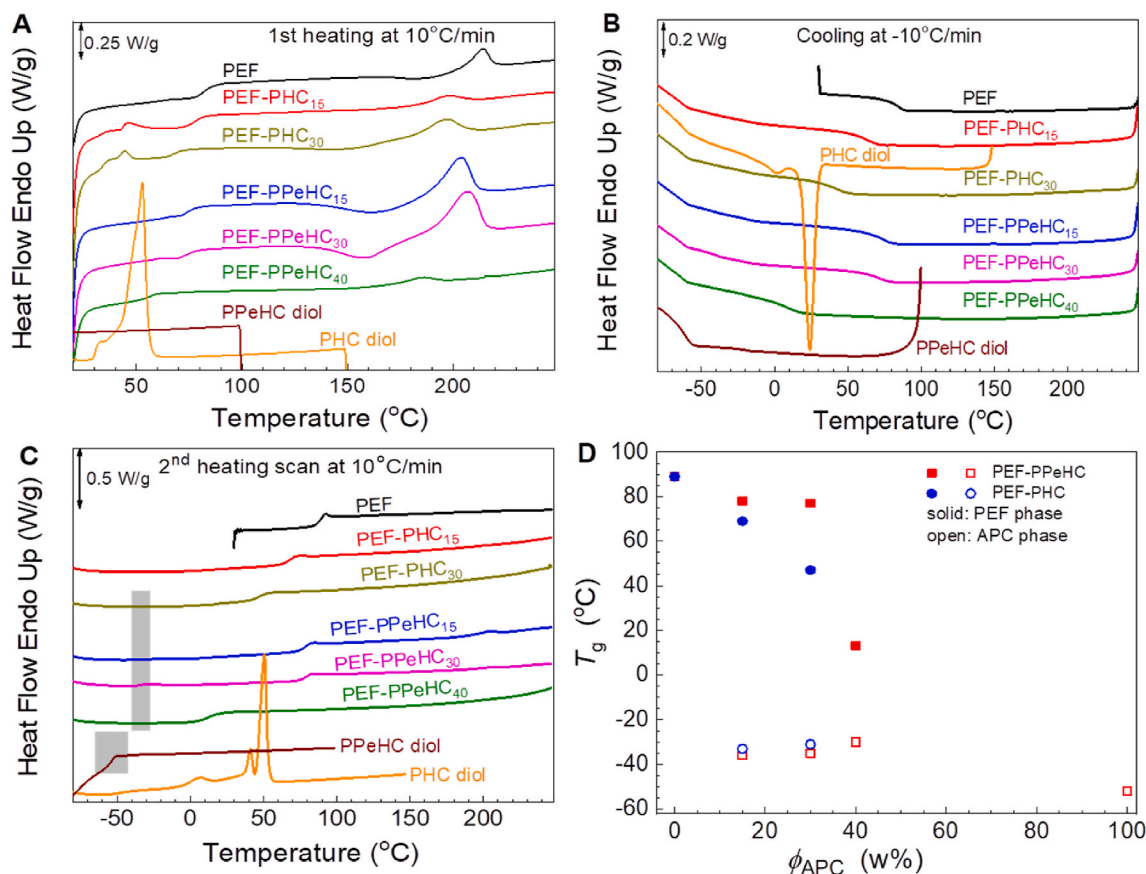
$$M_{\text{RC}} \text{ (for PPeHC)} = M_{\text{Pec}} \times (1 - \phi_{\text{HC}}) + M_{\text{HC}} \times \phi_{\text{HC}} \quad (3)$$

$$\phi_{\text{HC}} (\text{mol}\%) = \frac{I_{\text{g}}}{2I_{\text{f}} + I_{\text{g}}} \times 100\% \quad (4)$$

Two PEF samples with different intrinsic viscosities (IV, 0.50 and 0.82 dL/g) were synthesized via melt polycondensation. The sample with IV of 0.5 dL/g was used for modification. Its <sup>1</sup>H NMR spectrum is shown in Fig. 1. The chemical shifts of CH in furan ring and CH<sub>2</sub> in EG unit appear at 7.46 ppm (f) and 4.88 ppm (a), respectively. The

chemical shifts of the outer (b) and inner (c) CH<sub>2</sub> in diethylene glycol furancarboxylate (DEGF) repeat unit formed via etherification side reaction appear at 4.76 ppm and 4.25 ppm respectively. In addition, tiny signal of terminal hydroxyl neighbouring CH<sub>2</sub> (a') can be observed at 4.83 ppm. The molar percentage of DEGF unit was calculated to be 5.3 mol%.

The chain extension/coupling reaction was conducted at 230 °C, about 15 °C higher than the melting point of PEF (214.5 °C). During the reaction, clear pole-climbing phenomenon or Weissenberg effect was observed and the intrinsic viscosity grew from 0.50 dL/g of PEF to high values, 0.73–1.67 dL/g for PEF-PPeHC<sub>15-40</sub> and 0.81–0.83 dL/g for PEF-PHC<sub>15-30</sub>. Fig. 1 also shows the <sup>1</sup>H NMR spectra of two typical APC-modified PEF materials, PEF-PPeHC<sub>30</sub> and PEF-PHC<sub>30</sub>. Clearly, the main resonance signals of PEF and APCs remained, but the signals (a', d', e') related to the terminal hydroxyls in PEF and APC diols all disappeared, and the methylene protons (r) neighbouring the urethane groups formed by chain extension/coupling reaction appeared at 3.3 ppm. It is noted that the signals of methine protons in the furan ring remains the same as in the pristine PEF. This was similarly observed in the synthesis of PEF-*mb*-PTMG multiblock copolymers [20]. Differently, in our previously reported “randomized” copolymers (PEF-*r*-PPeHC)<sup>14</sup> as well as in random copolyesters (PEHF<sup>12</sup> and PEPeF<sup>13</sup>), the signals of methine protons in the furan ring did split into two peaks because of the different chemical environment of the methine protons in the furan rings connecting to different diol moieties. From the <sup>1</sup>H NMR results as well as growth of melt viscosity and IV values, it can be concluded that chain extension/coupling reaction of PEF and APC diols took place and PEF was chemically modified by the APCs, at least to some extent. Due to the rapid formation of urethane bonds in short time, there was no observable ester-carbonate exchange reaction occurred and therefore no randomized copolymers formed. Considering the simultaneous chain



**Fig. 2.** (A–C) DSC curves and (D) composition dependence of glass transition temperature ( $T_g$ ) of APC-modified PEFs.

**Table 2**  
Thermal properties of the APC diols, pristine PEF and APC-modified PEFs.

Sample	1st heating at 10 °C/min					cooling		2nd heating at 10 °C/min		
	$T_g^a$ (°C)	$T_{cc}^b$ (°C)	$\Delta H_{cc}^b$ (J/g)	$T_m^c$ (°C)	$\Delta H_m^c$ (J/g)	$T_c$ (°C)	$\Delta H_c$ (J/g)	$T_g^a$ (°C)	$T_m^c$ (°C)	$\Delta H_m^c$ (J/g)
PHC diol	Nd	nd	Nd	52.8	56.3	24.1	44.2	nd	50.5	41.2
PpHC diol	Nd	nd	Nd	nd	nd	nd	nd	-52	nd	nd
PEF (0.5 dL/g)	82	186	6.1	215	6.3	nd	nd	nd	nd	nd
PEF-PHC <sub>15</sub>	77	162	1.8	46.0,198 <sup>d</sup>	2.0,3.2 <sup>d</sup>	nd	nd	-33,69 <sup>d</sup>	nd	nd
PEF-PHC <sub>30</sub>	69	151	7.1	44.3,197 <sup>d</sup>	2.3,8.0 <sup>d</sup>	nd	nd	-31,47 <sup>d</sup>	nd	nd
PEF-PpHC <sub>15</sub>	73	164	16.4	204	16.6	nd	nd	-36,78 <sup>d</sup>	204	1.3
PEF-PpHC <sub>30</sub>	75	159	19.7	207	20.5	nd	nd	-35,77 <sup>d</sup>	205	0.4
PEF-PpHC <sub>40</sub>	56	nd	Nd	185.6	2.4	nd	nd	-30,13 <sup>d</sup>	nd	nd

<sup>a</sup> Glass transition temperature ( $T_g$ ).

<sup>b</sup> Cold crystallization temperature and enthalpy.

<sup>c</sup> Melt crystallization temperature and enthalpy.

<sup>d</sup>  $T_g$  of APC and PEF moieties.

extension and coupling reactions and the difference in reaction reactivity and concentration of PEF diol and APC diols with HDI, the products could not be only randomly segmented copolymers of PEF and APC but were actually a mixture or blend comprising segmented copolymers, chain extended APC, chain extended PEF and even some pristine PEF. The OH end groups in the APC diols are neighboring longer alkylene ( $\text{CH}_2$ )<sub>5-6</sub> and therefore have higher mobility and reactivity [13] than the end OH neighboring ethylene in the PEF diol. On the other hand, the concentration of end OH in the APC diols was clearly higher than that in PEF diol due to the lower molecular weight of the APC diols. For these two reasons, the chain-extension of the APC diols would be faster than that of the PEF diol and the chain-extended APCs might be formed preferentially.

The mass percentage of APC ( $\phi_{\text{APC}}$ ) in the products based on the sum of the mass of APC and PEF can be calculated from the <sup>1</sup>H NMR results with equation (5). As shown in Table 1, the results agreed well with the APC feeding ratio,  $\phi_{\text{APC}}$ . The DEGF content of PEF moiety in the products remained unchanged as compared with the pristine PEF. In PEF-PpHC, the  $\phi_{\text{HC}}$  values in PpHC segment can also be calculated with equation (4). The results also agreed well with that of the PpHC diol.

$$\phi_{\text{APC}}(w\%) = \frac{M_{\text{RC}}I_e}{M_{\text{EF}}I_a + M_{\text{DEGF}}I_c + M_{\text{RC}}I_e} \times 100\% \quad (5)$$

### 3.1.1. Thermal transition

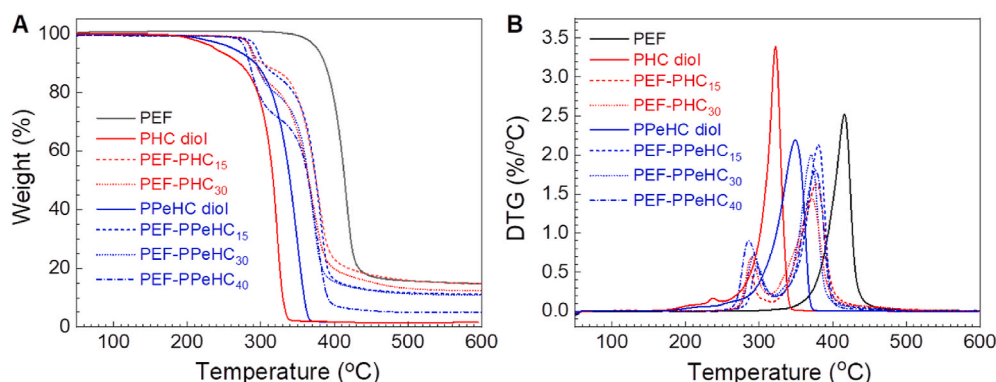
Like PEF with high IV [12,13,33], the PEF sample with relatively low IV (0.50 dL/g) was also weakly crystallizable. As shown in Fig. 2 and Table 2, it displayed weak cold crystallization ( $T_{cc}$  186 °C,  $\Delta H_{cc}$  6.1 J/g) and melting ( $T_m$  215 °C,  $\Delta H_m$  6.3 J/g) in the first heating scan at 10 °C/min, but neither melting nor crystallization was observed during the cooling and the second heating scans. The PHC diol showed clear melt crystallization peak ( $T_c$  24.1 °C,  $\Delta H_c$  44.2 J/g) and melting peak ( $T_m$  50.5 °C,  $\Delta H_m$  41.2 J/g) in the cooling and second heating scan,

respectively, and neither glass transition nor cold crystallization was observed, indicating its strong crystallizability [31]. But the PpHC diol is a fully amorphous prepolymer as there was only a glass transition observed in all DSC scans. The observed  $T_g$  (-52 °C) agrees well with the data reported by Feng et al. [31].

All the APC-modified PEFs were proved to be amorphous or weakly crystallizable. There was no melt crystallization peak in the cooling scan for all the materials. In the second heating scan, PEF-PpHC<sub>15</sub> and PEF-PpHC<sub>30</sub> exhibited very weak melting peak ( $\Delta H_m$  1.3-0.4 J/g at 204–205 °C). In the first heating scan, all the materials displayed clear melting. For PEF-PpHC<sub>15</sub> and PEF-PpHC<sub>30</sub>, the presence of PpHC seemed to promote the cold crystallization of PEF. As a result, stronger cold crystallization of PEF segment occurred at lower temperature ( $T_{cc}$  164-159 °C vs. 186 °C,  $\Delta H_{cc}$  16.4–19.7 J/g vs. 6.1 J/g) and the melting enthalpy ( $\Delta H_m$  16.6–20.5 J/g vs. 6.3 J/g, at  $T_m$  204–207 °C vs. 215 °C) increased as compared with the PEF diol. This is ascribed to partial miscibility between the APCs and PEF. In other words, the miscible part of APC plays a role of plasticizer to promote the chain mobility of PEF. Such partial miscibility and plasticization effect were supported by the two separate  $T_g$  values of PEF and APC and the decreasing  $T_g$  of PEF phase with  $\phi_{\text{APC}}$ , as shown in Fig. 2C and D. The glass transition of the APC microphases composed of chain-extended APC is very weak, as indicated by the shaded part in Fig. 2C. In addition, the crystallizability of PHC was strongly depressed after chain extension/coupling, therefore, only weak melting peak ( $T_m$  46.0-44.3 °C,  $\Delta H_m$  2.0-2.3 J/g) was observed in the first heating scan.

### 3.1.2. Thermal stability

Thermal stability of the products was investigated by TGA under N<sub>2</sub> atmosphere and compared with that of the APC diols and high molecular weight PEF (0.82 dL/g). The TGA and DTG curves are shown in Fig. 3, and some characteristic parameters including the decomposition



**Fig. 3.** TGA (A) and DTG (B) curves of the APC-modified PEFs, APC diols and high molecular PEF.

**Table 3**

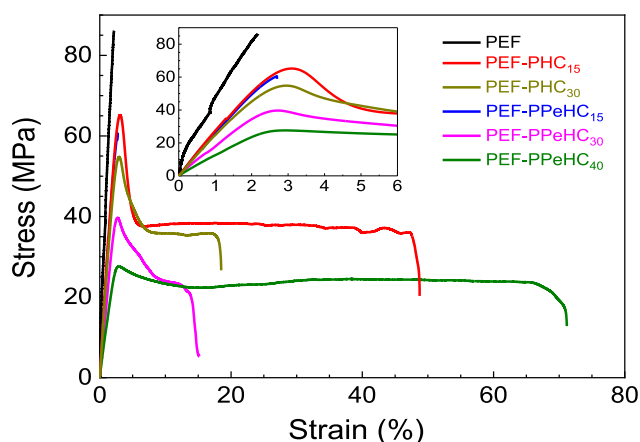
Thermal gravimetric analysis results of PEF and APC-modified PEFs measured at 10 °C/min under N<sub>2</sub> atmosphere.

sample	$T_{d,5}^a$ (°C)	$T_{d,max}^b$ (°C)	$R_{600}^c$ (wt %)
PEF	376	416	14.8
PHC diol	238	322	1.6
PPeHC diol	262	349	1.6
PEF-PHC <sub>15</sub>	287	286, 378	14.7
PEF-PHC <sub>30</sub>	285	290, 371	12.3
PEF-PPeHC <sub>15</sub>	295	297, 381	11.1
PEF-PPeHC <sub>30</sub>	288	293, 370	10.7
PEF-PPeHC <sub>40</sub>	279	285, 376	5.1

<sup>a</sup> Decomposition temperature at 5% weight loss.

<sup>b</sup> Decomposition temperature at maximum decomposition rate.

<sup>c</sup> Residual mass percentage at 600 °C.



**Fig. 4.** Typical tensile stress-strain curves of APC-modified PEFs.

temperatures at 5% weight loss ( $T_{d,5}$ ) and maximum decomposition rate ( $T_{d,max}$ ) and residual mass percentage at 600 °C ( $R_{600}$ ) are summarized in Table 3. Different from the single-stage decomposition and reasonably good thermal stability of the PEF, all the APC-modified PEFs showed two-stage decomposition and much poorer thermal stability. Obviously, the mass loss of the first stage corresponds to the degradation of APC moiety possibly via unzipping,  $\beta$ -H transfer and decarboxylation reactions [34] and therefore occurred very early ( $T_{d,max1}$ , 279–295 °C). For the APC diols, mass loss occurred at about 200 °C, suggesting poorer thermal stability because the presence of end OH groups in the APC diols induced unzipping via hydroxyl back-biting reaction [34]. When the end OH groups had been converted to the urethane bonds and the APC segments were chain-extended or coupled with PEF, the OH induced unzipping was depressed or avoided. As a result, the thermal stability of the products was improved and the starting decomposition temperature of the PEF-APC products were higher than that of the corresponding APC diols and high enough to endure the reaction temperature, 230 °C, at least for the short reaction time, 15 min. The second stage ( $T_{d,max2}$ , 370–381 °C) occurred earlier than PEF ( $T_{d,max}$  416 °C) and the

**Table 4**

Young's modulus ( $E$ ), yielding ( $\sigma_y$ ) and breaking ( $\sigma_b$ ) strength, elongation at yield ( $\epsilon_y$ ) and break ( $\epsilon_b$ ), notched izod impact strength ( $\sigma_i$ ) of PEF and APC-modified PEF materials.

Sample	$IV$ (dL/g)	$E$ (GPa)	$\sigma_y$ (MPa)	$\sigma_b$ (MPa)	$\epsilon_y$ (%)	$\epsilon_b$ (%)	$\sigma_i$ (kJ/m <sup>2</sup> )
PEF (0.82 dL/g)	0.81	3.43 ± 0.16	nd	84 ± 2	nd	3 ± 1	2.1 ± 0.1
PEF-PHC <sub>15</sub>	0.83	2.76 ± 0.35	65 ± 1	38 ± 2	3 ± 1	55 ± 11	4.0 ± 0.2
PEF-PHC <sub>30</sub>	0.81	2.52 ± 0.30	54 ± 2	35 ± 2	3 ± 1	18 ± 4	11.3 ± 2.2
PEF-PPeHC <sub>15</sub>	0.73	2.49 ± 0.22	nd	62 ± 4	nd	2 ± 1	3.5 ± 0.8
PEF-PPeHC <sub>30</sub>	1.05	1.87 ± 0.17	43 ± 4	22 ± 3	3 ± 1	19 ± 10	14.2 ± 2.8
PEF-PPeHC <sub>40</sub>	1.67	1.22 ± 0.12	24 ± 3	22 ± 2	3 ± 1	68 ± 10	78.1 ± 3.1

previously reported “randomized” PEF-*r*-PPeHC copolymers ( $T_{d,max}$  399–379 °C [14]). Owing to the poorer thermal stability of the APC segment, the thermal stability of the PEF-APC materials is inferior to that of the “randomized” PEF-*r*-PPeHC copolymers.

### 3.1.3. Mechanical properties

The tensile curves of PEF (0.82 dL/g) and the APC-modified PEFs are shown in Fig. 4 and the mechanical property data are summarized in Table 4. In comparison with the rigid and brittle PEF with high tensile strength (84 MPa) and modulus (3.4 GPa) but low ductility (3%, elongation at break) [12,13], all the products except PEF-PPeHC<sub>15</sub> behaved as ductile plastics, displaying obvious yielding and necking phenomena and improved ductility along with decreased modulus and strength. The brittle tensile behavior of PEF-PPeHC<sub>15</sub> might result from its relatively low IV (0.73 dL/g) because the PEF-PHC<sub>15</sub> sample with higher IV did display typical ductile tensile behavior with greatly improved elongation at break of 55%. With increasing APC content, it can be seen that both the tensile modulus and yielding strength decreased, but the elongation at break did not show clear composition dependence as it strongly depends on molecular weight which could not be controlled to be constant for all the samples. It can also be found that the PEF-PHC samples exhibited higher tensile modulus and yielding strength than the PEF-PPeHC ones with the same composition. This is ascribed to the remaining weak crystallization of PHC as compared with the fully amorphous PPeHC. Among them, PEF-PHC<sub>15</sub> displayed the best comprehensive tensile properties: greatly improved ductility (elongation at break 55%) and high modulus (2.8 GPa) and yielding strength (65 MPa).

In comparison with the brittle PEF, the presence of APC in the products endowed them with greatly improved impact toughness and became highly toughened materials. The notched izod impact strength increased from 2.1 kJ/m<sup>2</sup> of PEF to 3.5–4.0, 11.3–14.2 and 78.1 kJ/m<sup>2</sup> at APC content of 15 wt%, 30 wt% and 40 wt%, which is 1.7–1.9, 5.4–6.8 and 37.2 times than PEF, respectively.

To better understand the mechanical properties of the APC-modified PEF materials, the tensile and impact properties are compared with our previously reported PEF-*mb*-PTMG multi-block [20] and PEF-*r*-APC randomized [14] copolymers in Fig. 5. It can be seen that all of them possess comparable tensile modulus and maximum (yielding or breaking) strength at the same composition. But the PEF-*mb*-PTMG copolymers have clearly higher tensile ductility than the PEF-APC samples at 20 wt% or higher modifier content though the tensile ductility is comparable at 15 wt% modifier content. In contrast, when the impact toughness is concerned, it is found that the PEF-APC products behave even better than PEF-*mb*-PTMG, with earlier brittle-tough transition and higher toughness especially at low modifier content. For example, the impact strength kept unchanged even when 20 wt% PTMG was incorporated into the PEF-*mb*-PTMG copolymers, but incorporation of 15 wt% APC into PEF-APC improved the impact strength by about 1.8 times. On the other hand, the impact toughness of the PEF-*r*-APC was not improved when compared with PEF [14].

### 3.1.4. Impact fracture surface morphology

The morphology of the impact fracture surface of the PEF-APC

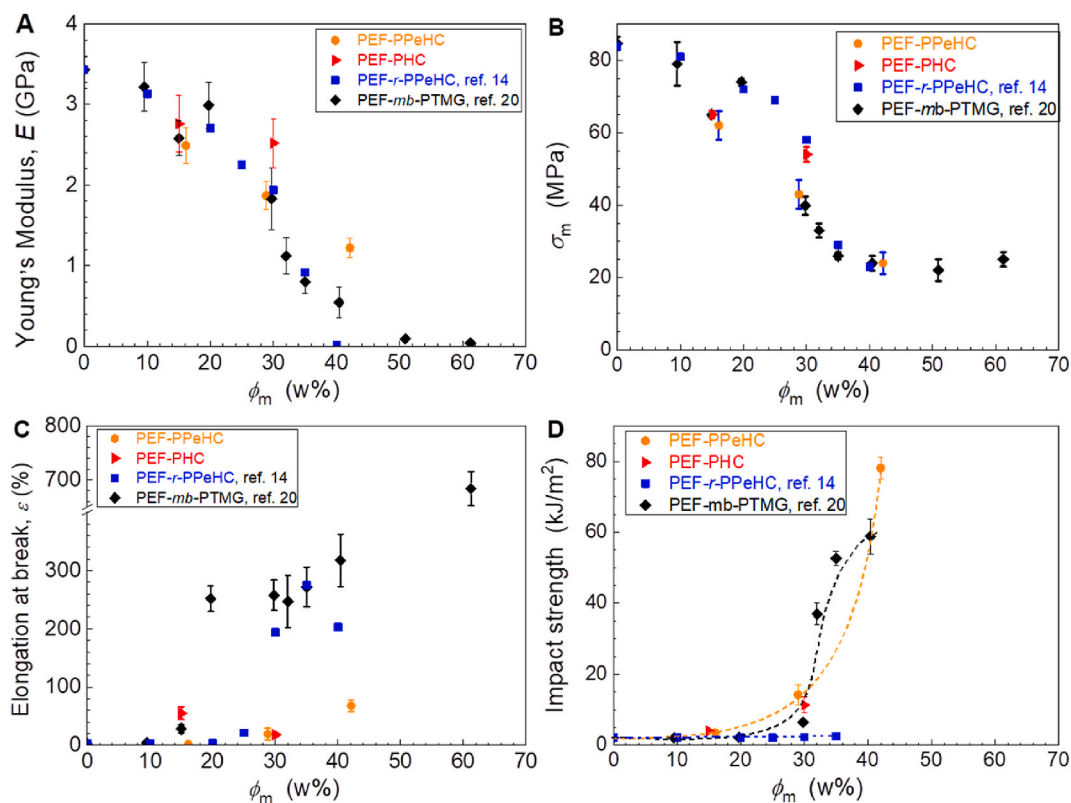


Fig. 5. Composition dependences of Young's modulus  $E$  (A), maximum tensile strength  $\sigma_m$  (B), elongation at break  $\epsilon_b$  (C), and notched izod impact strength  $\sigma_i$  (D) of PEF-APC, PEF-r-PPeHC [14] and PEF-mb-PTMG [20].

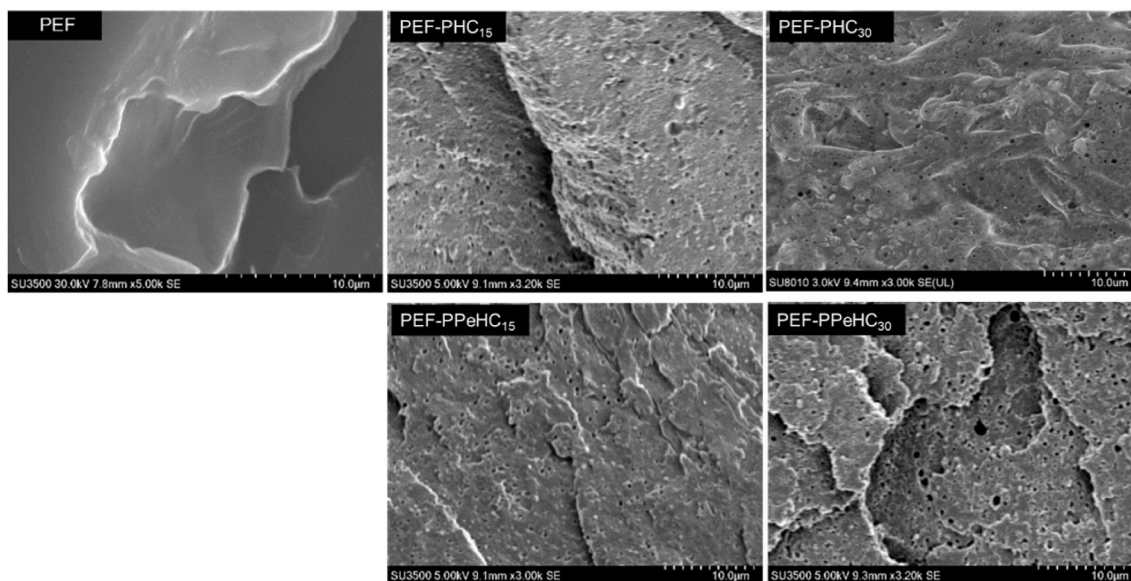


Fig. 6. Impact fracture surface morphology of PEF and four APC-modified PEFs: PEF-PHC<sub>15</sub>, PEF-PHC<sub>30</sub>, PEF-PPeHC<sub>15</sub> and PEF-PPeHC<sub>30</sub>.

materials containing 15 wt% or 30 wt% APC as well as PEF homopolymer (IV 0.82 dL/g) was observed with SEM and compared in Fig. 6. Different from the smooth fracture surface of PEF resulting from brittle fracture, coarse fracture surface was observed for all the APC-modified PEFs, indicating plastic deformation during impact testing. Furthermore, many pores with size of about 0.5–1  $\mu\text{m}$  was observed on the fracture surface. Such an observation supports the conclusion of microphase separation between chain-extended APC dispersed microphase and the PEF matrix. During impact testing, one can assume that a lot of

impact energy was dissipated to pull out the chain-extended APC microparticles from the PEF matrix, leaving the pores observed in the SEM micrographs.

### 3.1.5. Gas barrier properties

Finally, the gas barrier properties of PEF-PHC<sub>15</sub>, the sample with best and balanced mechanical properties, were assessed with O<sub>2</sub> and CO<sub>2</sub> permeation experiments at 23 °C using films prepared by hot pressing. As shown in Table 5, the O<sub>2</sub> and CO<sub>2</sub> permeation coefficients ( $P_{O_2}$  and

**Table 5**

Gas barrier properties of PEF-PHC<sub>15</sub>, PET, PEF and some other modified PEF materials.

Sample	$P_{O_2}$ (barrer)	$P_{CO_2}$ (barrer)	BIF <sub>O<sub>2</sub></sub>	BIF <sub>CO<sub>2</sub></sub>	Ref.
PEF-PHC <sub>15</sub>	0.021	0.024	1.05	5.0	this study
PEF	0.0041	0.012	5.4	10	This study
PET standard	0.022	0.12	1.0	1.0	this study
PEF- <i>mb</i> -PTMG <sub>20</sub> <sup>a</sup>	0.042	0.11 <sup>c</sup>	0.43	1.09	[20]
PEF- <i>r</i> -PPeHC <sub>25</sub> <sup>b</sup>	0.027	0.033	0.81	3.6	[14]

<sup>a</sup> PEF-*mb*-PTMG<sub>x</sub> multiblock copolymers with x wt% soft segment (PTMG) reported in ref. 20.

<sup>b</sup> PPeHC-modified randomized PEF copolymers reported in ref. 14.

<sup>c</sup> In ref. 20, only O<sub>2</sub> permeation coefficient was reported; the CO<sub>2</sub> permeation coefficient was measured in this study.

$P_{CO_2}$ ) of PEF-PHC<sub>15</sub> are 0.021 barrer and 0.024 barrer, respectively, being about five times and twice of those of the PEF homopolymer. Therefore, incorporating 15 wt% PHC significantly reduced the gas barrier properties of PEF. But when compared with the PET standard film ( $P_{O_2}$  0.022 barrer,  $P_{CO_2}$  0.12 barrer), PEF-PHC<sub>15</sub> displays comparable O<sub>2</sub> barrier (BIF<sub>O<sub>2</sub></sub> 1.05) and much better CO<sub>2</sub> barrier (BIF<sub>CO<sub>2</sub></sub> 5.0) properties. When compared with other modified PEF materials with improved impact toughness and/or ductility like PEF-*mb*-PTMG multiblock [20] and randomized PEF-*r*-PPeHC [14] copolymers, PEF-PHC<sub>15</sub> also displayed superior gas barrier properties.

#### 4. Conclusions

Aliphatic polycarbonates (APC) diols, including poly(1,6-hexylene carbonate) (PHC) and poly(1,5-pentylene-co-1,6-hexylene carbonate) (PPeHC) diols were used as modifiers to prepare APC-modified PEF materials, via chain extension/coupling of PEF and APC diols using hexamethylene diisocyanate (HDI) as chain extension/coupling agent. The products are weakly crystallizable in which PEF and APC were proved to be partially miscible with each other and therefore the PEF phase was plasticized by partial APC and its cold crystallization was promoted consequently. The APC-modified PEF materials containing 15–40 wt% APC displayed significantly enhanced tensile ductility and impact toughness. In comparison with the PEF-*mb*-PTMG multiblock copolymers, these materials showed inferior tensile ductility but superior gas barrier properties. In comparison with the randomized PEF-*r*-APC, they showed comparable gas barrier and tensile properties but superior impact toughness. Among them, PEF-PHC<sub>15</sub> displayed balanced and PET-comparable mechanical properties and superior CO<sub>2</sub> barrier performance.

#### CRedit authorship contribution statement

**Hongzhou Xie:** Methodology, Investigation, Resources, data treatment, Writing – original draft, Visualization. **Hongxu Meng:** Investigation, data treatment. **Linbo Wu:** Conceptualization, Methodology, Writing – review & editing, Supervision. **Bo-Geng Li:** Supervision. **Philippe Dubois:** Supervision.

#### 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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