Research Article

Wei Zhang, Qingyin Wang, Gongying Wang, and Shaoying Liu*

The effect of isothermal crystallization on mechanical properties of poly(ethylene 2,5-furandicarboxylate)

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Abstract: The effects of isothermal crystallization temperature/time on mechanical properties of bio-based polyester poly(ethylene 2,5-furandicarboxylate) (PEF) were investigated. The intrinsic viscosity, crystallization properties, thermal properties, and microstructure of PEF were characterized using Ubbelohde viscometer, X-ray diffraction, polarizing optical microscope, differential scanning calorimetry, and scanning electron microscopy. The PEF sample isothermally crystallized at various temperatures for various times was denoted as PEF-*T-t*. The results showed that the isothermal crystallization temperature affected the mechanical properties of PEF-*T-30* by simultaneously affecting its crystallization properties and intrinsic viscosity. The isothermal crystallization time only affected the crystallization properties of PEF-110-*t*. The crystallinity of PEF-110-40 was 17.1%. With small crystal size, poor regularity, and α' -crystal, PEF-110-40 can absorb the energy generated in the tensile process to the maximum extent. Therefore, the best mechanical properties can be obtained for PEF-110-40 with the tensile strength of 43.55 MPa, the tensile modulus of 1,296 MPa, and the elongation at a break of 13.36%.

Keywords: bio-based polyester, crystallization temperature, crystallization time, mechanical properties, PEF

1 Introduction

Poly(ethylene 2,5-furandicarboxylate) (PEF) was obtained from biomass raw materials 2,5-furan dicarboxylic acid (or 2,5-furan dicarboxylate) and ethylene glycol by melt polycondensation. With the advantages of abundant raw materials, good heat resistance, and outstanding barrier performance, PEF has broad application prospects in the field of packaging materials and attracted extensive attention in recent years (1–4).

Nevertheless, the drawbacks of PEF, such as poor toughness, slow crystallization rate, dark color, and low molecular weight, have limited its industrial application, so it has not been commercialized yet to date. Esterification polycondensation (5–8) and transesterification polycondensation (9–13) are the main routes to synthesize PEF. The current research mainly focuses on the study of synthesis process parameters (7,13), copolymerization (8,14–25), and nanocomposite (26–29) to improve molecular weight, reduce the chroma of the product, control the crystallization properties, and improve the mechanical properties. Knoop et al. (9) prepared high molecular weight furan dicarboxylic acid-based polyester via melt polymerization followed by solid-state polycondensation and studied the crystallization properties of high molecular weight PEF. The results showed that the molecular weight reached $83,000 \text{ g}\cdot\text{mol}^{-1}$, crystallization occurs between 110°C and 200°C, and the crystallization rate was the fastest between 150°C and 160°C. Wu et al. (12) prepared PEF via transesterification polycondensation using organic nonmetal 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) as a catalyst and studied its isothermal crystallization and nonisothermal crystallization kinetics. The results showed that PEF exhibited rapidly melt crystallization behavior in both nonisothermal and isothermal manners. When the cooling rate of nonisothermal crystallization was $10^\circ\text{C}\cdot\text{min}^{-1}$, the melt crystallization rate was the fastest at 160°C with a minimum melt crystallization half-life (1.6 min). After complete isothermal crystallization at 160–210°C, the crystallinity was

* Corresponding author: Shaoying Liu, Green Chemical Division, Chengdu Institute of Organic Chemistry, Chinese Academy of Sciences, Chengdu, Sichuan, 610041, China, e-mail: lsy741090720@163.com

Wei Zhang: Green Chemical Division, Chengdu Institute of Organic Chemistry, Chinese Academy of Sciences, Chengdu, Sichuan, 610041, China; Department of Materials Engineering, Taiyuan Institute of Technology, Taiyuan, Shanxi, 030008, China; University of Chinese Academy of Sciences, Beijing, 100049, China

Qingyin Wang, Gongying Wang: Green Chemical Division, Chengdu Institute of Organic Chemistry, Chinese Academy of Sciences, Chengdu, Sichuan, 610041, China

27–34%. Stoclet *et al.* (30) studied the relationship between isothermal crystallization temperature and crystal form of PEF. The results showed that the transformation of crystal form occurred near 170°C. When the crystallization temperature T_c was below 170°C, the irregular α' -crystal was formed. When the crystallization temperature T_c was above 170°C, the regular α -crystal could be formed. Furthermore, Tsanaktsis *et al.* (31) showed that there existed three types of crystals: α , α' , which were formed during melt or cold-crystallization at various temperature ranges, and β -crystal type that was formed upon solution crystallization of PEF. Mao *et al.* (32) and Maini *et al.* (33) deeply determined the crystal structure of PEF using fiber and powder patterns, respectively. Lotti *et al.* (27) *in situ* prepared PEF nanocomposites with multi-walled carbon nanotubes (MWCNTs) and graphene oxide (GO) via melt polycondensation. The effects of crystallization mode and nanoparticle type on the crystal form of PEF were investigated. The results showed that the pure PEF produced β -crystal after solvent treatment, while α -crystal formed after melt or cold-crystallization, but PEF nanocomposites could singly form α -crystal. Wang *et al.* (14,34) used 2,2,4,4-tetramethyl-1,3-cyclobutanediol (CBDO) as copolymerization modifier to study the effect of modifier dosage on the properties of PEF. The results showed that CBDO could improve the transparency and mechanical properties of PEF, but the barrier property decreased.

In this paper, PEF was prepared by the esterification polycondensation method. The relationship between crystallization temperature/time and crystallization behavior of PEF, such as crystallization rate, crystal form, crystal morphology, and crystallinity, as well as the relationship between crystallization behavior and mechanical properties was investigated. The results can provide a method and theoretical reference for the modification and post-processing of PEF.

2 Experimental

2.1 Materials and instruments

2,5-furandicarboxylic acid (FDCA, 98%) was purchased from Shanghai Macklin Biochemical Co., Ltd. (China). Ethylene glycol (EG, 99%) and phenol (C_6H_5OH , 99%) were purchased from Guangdong Guanghua Technology Co., Ltd. (China). Dibutyltin oxide (DBTO, 98%) was purchased from Acros organizations. 1,1,2,2-tetrachloroethane ($C_2H_2Cl_4$, 99%) was purchased from Chengdu Kelong Chemical Co., Ltd. (China). All the chemicals were used as received.

Molding machine (SY-6210A, Dongguan Shiyan Precision Instrument Co., Ltd.), Universal testing machine (NKK 3010D, Shenzhen Nanfang Jingke Instrument Equipment Co., Ltd.), Scanning electron microscope (JSM-7200F, JEOL, Japan), Differential scanning calorimeter (DSC Q20, TA, USA), X-ray diffractometer (Smartlab X-ray Diffractometer, RIGAKU, Japan), and Polarizing microscope (BX41, Olympus, Japan) were used.

2.2 Synthesis of PEF

PEF was synthesized via the esterification-polycondensation method. FDCA and EG at a molar ratio of diacid/diol = 1:1.8 were added into the reactor equipped with a mechanical stirrer, N_2 inlet, and reflux condenser, and DBTO (0.15 mol% based on FDCA) was used as a catalyst. The air in the reactor was purged with nitrogen for three times, and the esterification was carried out at 200°C under nitrogen protection. After almost all the theoretical amount of water was distilled out, gradually increasing the temperature to 230°C, reducing the reaction pressure below 100 Pa within 30 min, and keeping this condition for 4 h, PEF was prepared with an intrinsic viscosity of $0.44 \text{ dL}\cdot\text{g}^{-1}$.

2.3 Preparation of samples

Samples were prepared by compression molding, the molding temperature, pressure, and time were 190°C, 10 MPa, and 2 min, respectively. Then, the samples were transferred rapidly to the water-cooling plate of the molding machine to obtain amorphous samples (named PEF, $0.36 \text{ dL}\cdot\text{g}^{-1}$).

Preparation of samples with various crystallization temperatures: The samples with various crystallization temperatures were prepared by isothermal crystallization of amorphous samples in the blast oven at 90°C, 110°C, 120°C, 130°C, 150°C, 170°C, and 190°C for 30 min, respectively, and marked as PEF- T -30 ($T = 90^\circ\text{C}$, 110°C , 120°C , 130°C , 150°C , 170°C , and 190°C).

Preparation of samples with various crystallization times: The samples with various crystallization times were prepared by isothermal crystallization for 10, 20, 30, 40, 50, 60, and 720 min in a blast oven at 110°C corresponding to the optimal mechanical properties and marked as PEF-110- t ($t = 10, 20, 30, 40, 50, 60$, and 720).

The intrinsic viscosity of the crystallized samples did not decrease obviously until the crystallization temperature reached 190°C (PEF-190-30, $0.32 \text{ dL}\cdot\text{g}^{-1}$).

2.4 Characterization

The tensile properties of PEF with various crystallization temperatures and times were tested according to ISO 527-2:1993, with a tensile rate of $10 \text{ mm} \cdot \text{min}^{-1}$. The tensile specimens were dumbbell-shaped with the dimension of 1 mm in thickness and 2 mm in neck width. All samples were conditioned at room temperature for at least 48 h before testing.

A scanning electron microscope (SEM) was used to characterize the micromorphology of the tensile sections of the samples. The accelerating voltage was 10 kV, and the sections were sprayed with gold before SEM analysis.

The intrinsic viscosity of samples was tested by Ubbelohde viscometer at $25 \pm 2^\circ\text{C}$ according to GB/T 14190-2008. Phenol/1,1,2,2-tetrachloroethane with a mass ratio of 1:1 was used as the mixed solvent.

The thermal and crystallization characteristics of PEF samples with various crystallization temperatures and time were measured by differential scanning calorimetry (DSC) and calibrated by indium and zinc standards. About 5 mg of the sample was put into an aluminum pot and heated from 30°C to 250°C at a heating rate of $10^\circ\text{C} \cdot \text{min}^{-1}$ under the N_2 protection ($40 \text{ mL} \cdot \text{min}^{-1}$). The crystallinity was calculated according to Eq. 1:

$$X_c = \frac{\Delta H_m - \Delta H_{cc}}{\Delta H_m^0} \times 100\% \quad (1)$$

where ΔH_m is the enthalpy of melting, ΔH_{cc} is the enthalpy of cold crystallization, and ΔH_m^0 is the theoretical melting enthalpy of 100% crystalline PEF, $\Delta H_m^0 = 137 \text{ J} \cdot \text{g}^{-1}$ (35). Furthermore, isothermal crystallization of PEF from the melt was studied at a crystallization temperature range from 90°C to 190°C . The temperature was raised from 30°C to 250°C at the rate of $10^\circ\text{C} \cdot \text{min}^{-1}$, kept for 2 min to eliminate the heat history, then rapidly lowered to the isothermal crystallization temperature (T_c) at the rate of $50^\circ\text{C} \cdot \text{min}^{-1}$ for a certain period of time.

X-ray diffraction (XRD) was used to test the crystallinity and crystal form of the samples, with Cu K α radiation ($\lambda = 0.154 \text{ nm}$) in the angle 2θ range from 5° to 40° , tube voltage of 45 kV, and tube current of 200 mA. The crystal morphology and quantity of PEF were observed by polarized optical microscopy (POM) with X-8 hot stage and the magnification of $200\times$.

3 Results and discussion

3.1 Effect of crystallization temperature on PEF properties

3.1.1 XRD and POM analysis of PEF-T-30

PEF-T-30 with various crystallization temperatures for 30 min were measured by XRD and POM to analyze the effects of crystallization temperature on crystal form, crystallinity, and crystal morphology. The results are shown in Figure 1 and Figure A1 (in Appendix). Figure 1 shows that the XRD curves of untreated sample PEF and PEF-90-30 are shown typical amorphous peaks. The amorphous halo around 10° is the background peak. There is a weak diffraction peak at the crystallization temperature of 110°C . With the temperature continues to rise, the intensity of diffraction peaks at 2θ of 15.8° , 17.7° , 20.5° , 23.2° , and 26.5° increases gradually (The crystal planes have been shown in the XRD patterns) and tends to equilibrium after 170°C . The positions of these peaks are almost identical, which indicates a similar unit cell structure (36). Moreover, a new diffraction peak at 2θ of 19.1° appears at the crystallization temperature above 150°C , indicating a kind of more perfect crystalline form of PEF induced. Similar behavior has been observed by Stoclet et al. (30,37) and Maini et al. (33). The more perfect crystalline form is named α -crystal while the defective one is named α' -crystal. The results show that the crystallinity and the regularity of crystal structure of PEF-T-30 increase with the increase

Figure 1: XRD patterns of PEF-T-30.

of crystallization temperature, and α' -crystal transforms to α -crystal at 150°C.

Figure A1 shows that there is no crystal in the untreated sample (Figure A1a) and a few small spherulites appear after crystallization at 110°C (Figure A1b). With the increase of crystallization temperature, the number of spherulites increases significantly, especially after crystallization at 150–190°C. PEF-170-30 has the largest number of spherulites. The crystal size is so small that the change of size is not obvious when it is magnified 200 times. Papageorgiou *et al.* (35) also reported that PEF exhibits a large nucleation density and a small spherulite size even at high crystallization temperatures of 210°C.

3.1.2 DSC analysis of PEF-T-30

The DSC heating curves of PEF-T-30 are shown in Figure 2, and the thermal properties are summarized in Table A1 (in Appendix). It shows that with the increase of isothermal crystallization temperature, the glass transition temperature (T_g) of PEF-T-30 moves to the high-temperature region, the crystallization peak weakens, and the melting peak temperature (T_m) does not change significantly. The glass transition and crystallization peak disappear when the crystallization temperature exceeds 110°C, indicating high crystallinity. When the crystallization temperature reaches 150°C, a smaller melting peak of the secondary crystal appears. With the increase of the crystallization temperature, the melting peak of the secondary crystal shifts linearly to the high-temperature direction, and the strength remains unchanged. Combined with Figure 1, it is indicated that the crystallinity of PEF increases with the increase of crystallization temperature and then tends to be flat, but the crystallization temperature has little effect on the melting temperature. When the crystallinity

Figure 2: DSC heating curves of PEF-T-30.

increases to a certain extent, the secondary crystal will occur. The secondary crystal lamella is formed between the primary crystal lamella, and the physical hindrance in the formation process makes these crystal lamellae thinner, resulting in the melting temperature of the secondary crystal being lower than that of the primary crystal. The same observations were reported in the studies of Stoclet *et al.* (30,37) and van Berkel *et al.* (38).

3.1.3 Mechanical properties of PEF-T-30

The stress–strain curves of PEF-T-30 are shown in Figure 3, and the mechanical properties are shown in Table A2. It shows that the PEF-T-30 samples do not yield during the tensile process, which is a typical brittle fracture. The tensile strength, modulus, and elongation at break of PEF-T-30 first increase and then decrease with the increase of crystallization temperature. The tensile strength and elongation at the break of PEF-110-30 are the highest, which is twice as high as that of non-isothermal crystallization PEF. Combined with Figures 1 and 2, it is shown that the mechanical properties of PEF-T-30 are closely related to crystallinity, crystal regularity. The crystals allow the initiation and propagation of shear deformation more easily and then enhance the energy dissipating processing, and the mechanical properties are improved effectively with the increase of crystallinity. However, when the crystallinity reaches a certain degree, a large number of crystals tend to produce stress concentration during the tensile process, resulting in the decline of mechanical properties. The crystallinity of PEF-110-30 is 14.1% with small crystal size, poor regularity, mainly α' -crystal, which can absorb the energy generated in the tensile process to the maximum extent, so it gets the best mechanical properties. Compared with PEF-170-30 and PEF-190-30, although the crystallinity is

Figure 3: Tensile stress–strain curves of PEF-T-30.

similar, the mechanical properties of PEF-190-30 decrease, which is mainly due to the decrease of the intrinsic viscosity and the improvement of its crystal regularity.

The tensile sections of PEF, PEF-110-30, PEF-130-30, and PEF-150-30 were characterized by SEM, and the results are shown in Figure A2. The tensile cross-section of PEF without isothermal crystallization (Figure A2a) is relatively regular, the irregularity of tensile section of PEF-110-30 (Figure A2b) with crystallization at 110°C increases, and uniform deformation traces appear. The tensile section of PEF-130-30 (Figure A2c) tends to be flat and deformed locally. PEF-150-30 (Figure A2d) shows a flat section, and a large number of particles and micro pits with a diameter of about 1 μm appear on the surface which may be caused by the separation of the crystalline phase from the amorphous region. These changes in surface fracture correlate with the mechanical properties results.

3.2 Effect of crystallization time on PEF properties

3.2.1 XRD and POM analysis of PEF-110-*t*

To analyze the effects of crystallization time on crystal form, crystallinity, and crystal morphology, the PEF-110-*t* with various crystallization times at 110°C was measured by XRD and POM. The results are shown in Figure 4 and Figure A3. It can be seen from Figure 4 that the XRD pattern of PEF shows amorphous peaks. Weak characteristic diffraction peaks appear in the XRD pattern of PEF-110-20. With the increase of crystallization time, the intensity of diffraction peaks enhance, there are obvious diffraction peaks in PEF-110-720 pattern. However, there is

no characteristic diffraction peak near 19.1° which belongs to α -crystal. The results show that the α' -crystal with poor regularity is mainly formed during isothermal crystallization at 110°C.

Figure A3 shows that a small number of small spherulites appear after crystallization for 40 min (Figure A3b). With the increase of crystallization time, spherulites size and the number increase slowly, and a large number of spherulites appear in PEF-110-720 (Figure A3d). The results indicate that PEF crystallizes slowly at 110°C.

3.2.2 DSC analysis of PEF-110-*t*

The DSC heating curves of PEF-110-*t* with various crystallization times at 110°C are shown in Figure 5, and the thermal properties are summarized in Table A3. It shows that the crystallization peak of PEF-110-*t* weakens, while the melting enthalpy (ΔH_m) increases with the extension of crystallization time, indicating that the crystallinity is improved. There is no crystallization peak on the heating curve of PEF-110-720, indicating that the crystallization reaches saturation, and the saturation crystallinity is 45.4%. A small melting peak also appears around 130°C when the crystallization time exceeds 60 min. Combined with Figure 4, it is proved that this peak is the melting peak of the secondary crystal.

3.2.3 Mechanical properties of PEF-110-*t*

The stress–strain curves of PEF-110-*t* are shown in Figure 6, and the mechanical properties are shown in Table A4. It shows that brittle fracture occurs in PEF-110-*t*. With the extension of crystallization time, the tensile strength and elongation at break first increase and then decrease, and

Figure 4: XRD patterns of PEF-110-*t*.

Figure 5: DSC heating curves of PEF-110-*t*.

Figure 6: Tensile stress–strain curves of PEF-110-*t*.

PEF-110-40 reaches the highest with 115% and 128% higher than that of uncrystallized PEF, respectively. Tensile modulus increases gradually, and PEF-110-720 shows the highest modulus. Combined with Figures 4 and 5, it shows that the mechanical properties of PEF-110-*t* are closely related to crystallinity. PEF-110-40 gets the best mechanical properties, while the crystallinity is 17.1% with a small crystal size and moderate crystal number.

The tensile sections of PEF, PEF-110-20, PEF-110-40, and PEF-110-60 are shown in Figure A4. The tensile section of PEF-110-20 (Figure A4b) shows coarser fracture than that of PEF, and large deformation traces appear locally. PEF-110-40 (Figure A4c) shows the largest deformation traces and obvious stress whitening. The regularity of PEF-110-60 (Figure A4d) is improved with reduced deformation. The results show that with the extension of crystallization time, the irregularity of the PEF fracture surfaces increases first and then decreases, which is consistent with the results of mechanical properties.

Figure 7: DSC isothermal crystallization curves at different crystallization temperatures.

3.3 Isothermal crystallization of PEF

DSC isothermal crystallization curves at different crystallization temperatures are shown in Figure 7. It shows that there is no obvious crystallization before isothermal crystallization temperature below 130°C within 1 h. When the isothermal crystallization temperature ranges from 130°C to 190°C, the crystallization peak appears, and PEF crystallizes fastest at 170°C. To investigate whether PEF crystallizes at 110°C, the crystallization time is extended to 720 min, as shown in the embedded figure, and the crystallization peak appears in the curve. It indicates that PEF can be crystallized at 110°C, but the crystallization rate is extremely slow.

4 Conclusion

PEF was prepared via the direct esterification method, and the effects of isothermal crystallization temperature and time on the properties of PEF were investigated. The results reveal that the isothermal crystallization temperature affects the mechanical properties of PEF-T-30 by affecting its crystallization properties and intrinsic viscosity. With the increase of crystallization temperature, the crystallinity of PEF-T-30 increases with the increase of crystallization temperature, the regularity of crystal structure increases too, and α' -crystal with poor regularity transforms to α -crystal with good regularity at 150°C. Only small spherulites of PEF are obtained by isothermal crystallization at a temperature range from 90°C to 190°C. The isothermal crystallization time only affects the crystallization properties of PEF-110-*t*. With the extension of crystallization time, the crystal number and size of PEF-110-*t* increase, and the saturated crystallinity of PEF with crystallization temperature of 110°C is 45.4%. The secondary crystallization of PEF occurs with either increasing crystallization temperature or prolonging crystallization time. With small crystal size, poor regularity, α' -crystal, and the crystallinity of 17.1%, PEF-110-40 can absorb the energy generated in the tensile process to the maximum extent. Therefore, the best mechanical properties can be obtained for PEF-110-40 with the tensile strength of 43.55 MPa, the tensile modulus of 1,296 MPa, and the elongation at a break of 13.36%.

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Appendix

Table A1: Thermal properties of PEF-*T*-30

Samples	T_g (°C)	T_{cc} (°C)	ΔH_{cc} (J·g ⁻¹)	T_{m1} (°C) ^a	T_{m2} (°C) ^b	ΔH_m (J·g ⁻¹)	X_c (%)
PEF	73.6	153.8	32.5	ND	214.4	36.8	3.1
PEF-90-30	75.6	161.2	29.3	ND	215.3	35.9	4.8
PEF-110-30	81.5	155.6	10.8	ND	214.7	30.1	14.1
PEF-130-30	ND ^c	ND	ND	ND	215.2	36.5	26.6
PEF-150-30	ND	ND	ND	153.4	214.6	42.1	30.7
PEF-170-30	ND	ND	ND	171.0	214.3	47.2	34.5
PEF-190-30	ND	ND	ND	190.5	216.5	46.6	34.0

^a T_{m1} : melting temperature of the secondary crystal; ^b T_{m2} : melting temperature of the primary crystal; ^cND is non peak.

Table A2: Mechanical properties of PEF-*T*-30

Samples	Strength (MPa)	Modulus (MPa)	Elongation at break (%)
PEF	20.28	1,240	5.87
PEF-90-30	29.10	1,151	11.34
PEF-110-30	41.12	1,255	11.64
PEF-120-30	31.10	1,640	8.30
PEF-130-30	21.99	1,511	6.28
PEF-150-30	16.87	1,193	4.76
PEF-170-30	16.16	1,210	4.76
PEF-190-30	13.84	1,284	3.24

Table A3: Thermal properties of PEF-110-*t*

Samples	T_g (°C)	T_{cc} (°C)	ΔH_{cc} (J·g ⁻¹)	T_{m1} (°C)	T_{m2} (°C)	ΔH_m (J·g ⁻¹)	X_c (%)
PEF	73.6	153.8	32.5	ND	214.4	36.8	3.1
PEF-110-20	81.1	163.4	20.8	ND	214.7	30.2	6.9
PEF-110-40	81.8	158.5	19.8	ND	215.6	43.2	17.1
PEF-110-60	82.6	158.9	15.3	130.6	214.5	44.3	21.2
PEF-110-720	90.6	ND	ND	134.9	214.7	62.2	45.4

Table A4: Mechanical properties of PEF-110-*t*

Samples	Strength (MPa)	Modulus (MPa)	Elongation at break (%)
PEF	20.28	1,240	5.87
PEF-110-10	26.33	1,249	5.67
PEF-110-20	33.82	1,148	8.71
PEF-110-30	41.12	1,255	11.64
PEF-110-40	43.55	1,296	13.36
PEF-110-50	36.71	1,409	11.14
PEF-110-60	28.57	1,341	7.19
PEF-110-720	21.53	1,457	4.66

Figure A1: POM photos of PEF-T-30: (a) PEF, (b) PEF-110-30, (c) PEF-130-30, (d) PEF-150-30, (e) PEF-170-30, and (f) PEF-190-30.

Figure A2: SEM photos of tensile section of PEF-T-30: (a) PEF, (b) PEF-110-30, (c) PEF-130-30, and (d) PEF-150-30.

Figure A3: POM photos of PEF-110-*t*: (a) PEF, (b) PEF-110-40, (c) PEF-110-60, and (d) PEF-110-720.

Figure A4: SEM photos of tensile section of PEF-110-*t*: (a) PEF, (b) PEF-110-20, (c) PEF-110-40, and (d) PEF-110-60.