Supplementary Information

Preparation of Copolyester Elastomer by Introducing Lactic Acid-based Monomer with Enhaced Mechiancal Properties via Micro-crosslinking

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Contents:

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Total number of figures: 6

Total number of tables: 5

Characterization

Nuclear Magnetic Resonance (NMR). The structure and constituents of PBLxTy copolyesters were investigated using ^{1}H-NMR and ^{13}C-NMR on a Bruker AVAVCE NEO 600 NMR spectrometer at room temperature (25 ℃) in $CDCl_3$ as solvent.

Gel Permeation Chromatography (GPC). The molecular weight and distribution of PBLxTy copolyesters were determined using a GPC (Agilent PL-GPC220) coupled with two 300*7.5 mm PLgel 5 mm Mixed-D columns. Elution solvent was HPLC grade chloroform at 40 ℃ with a flow rate of 1.0 mL/min, and molecular weight was measured using polystyrene standard (3070-258,000 g/mol). The sample concentration was approximately 1.0 mg/mL.

Differential Scanning Calorimetry (DSC). Differential scanning calorimetry (DSC) measurements were performed on a Mettler-Toledo DSC I machine using the standard heating-cooling-heating temperature program in N_2 flux. The heating or cooling rate was 10 °C min^{-}, and the thermal history removal duration was 5 mins. For measurements, approximately 5-8 mg of the material was enclosed in aluminum crucibles, and all heating and cooling curves were recorded for further study. The temperature was then raised to 150 °C at a rate of 10 °C/min.

Thermo-Gravimetric Analysis (TGA). The thermal stability was determined by thermogravimetric analysis (Mettler-Toledo TGA/DSC), weighing 5-6 mg samples under N_2 and Air atmosphere with a 40 mL/min flow rate, respectively. The TGA curve was traced as the sample was heated from 50 to 800 ℃ at a heating rate of 20 ℃ /min.

Mechanical Tests. The tensile strength, tensile modulus and elongation at break

were tested at room temperature using an Instron 5567 tensile testing machine (Zwick/Roell Z1.0) with a 1KN load cell at extension rates of 100 mm/min. Hot press-molding was also used to prepare dumb-bell samples with dimensions of 20.0 mm (length) × 2.0 mm (neck width) × 1.0 mm (thickness).

Based on the cycling loading and unloading of the samples, cyclic tensile testing was utilized to examine the elastic recovery capabilities of PECSX-Y samples. The samples were stretched to ε_m=200% elongation at 25 °C at a stretching rate of 100 mm/min in a complete loop method. Subsequently, the cross-head retract with a 50mm/min shrinkage rate, until the standard load was 0 N, repeat the above two steps 5 times. The shape recovery rate (R_r) of PECSX-Y samples was obtained according to equation (1).

$$R_r(N) = \frac{\varepsilon_m - \varepsilon_p(N)}{\varepsilon_m - \varepsilon_p(N-1)} \qquad \text{* MERGEFORMAT (1)}$$

where N is the number of cycles, ε_m is the maximum strain of samples, $\varepsilon_p(N)$ and $\varepsilon_p(N\text{-}1)$ are the strains of PECSX-Y samples in two continuous cycles when the standard load is 0 N, and R_r(N) represents the elastic recovery rate of the Nth cycle.

Small Angle X-ray Scattering (SAXS). SAXS measurements were carried out using a Xenocs X-ray small angle Scatterometer (Xeuss 3.0, France) using monochromatic light with a wavelength of 0.15 nm. The sample detector distance was 1200 mm. Bragg's rule relates the position of the peak q max to the long period L: $L=2\pi/q_{max}$, where q, the scattering vector, λ is defined as q=4(sin θ)/λ, where θ is the X-ray wavelength, and is half of the scattering angle (2θ).

The material is degraded in an enzymatic environment at 37 °C using a phosphate

buffer solution (pH = 7.40) containing 0.1 mg/mL of CALB. The first sampling and weighing are carried out after two weeks of degradation. After that, sampling is conducted once every week. The samples are thoroughly rinsed three times with deionized water and then vacuum-dried to a constant weight in a vacuum oven at 40 °C.

A composting degradation experiment is carried out under the conditions of 58 °C and 50% humidity. The degradation solution and the nutrient soil used for composting are replaced weekly to prevent the inactivation of CALB enzyme and maintain the activity of microorganisms in the nutrient soil. The remaining weight of the sample after drying to a constant weight is used to determine the mass change. Subsequently, SEM (EV018, Carl Zeiss) is performed on the sample to observe the morphological changes during the degradation process.

Cytotoxicity Assay: The cytotoxicity of the PBLT films was evaluated by assessing cell viability. Circular samples, each 14 mm in diameter, were cut from the films and sterilized. These sterilized films were then placed in a sterile 24-well culture plate containing DMEM culture medium and pre-incubated overnight in a cell culture incubator. The following day, fibroblasts (ZQ 0450, Zhongqiao Xinzhou Biotech, Shanghai, China) in optimal growth conditions were seeded onto the films. After the cells adhered to the films and began to proliferate, their viability was measured at 24-hour intervals over three days using the Cell Counting Kit-8 (CCK-8) assay. For each measurement, 10 μL of CCK-8 solution was added to each well, followed by a 2-hour incubation at 37 ℃ (n = 3). A control group of cells cultured without films was also

included. After incubation, an appropriate volume of the supernatant was transferred to a 96-well plate, and the optical density (OD) was measured at 450 nm using a multifunctional microplate spectrophotometer.

Hemolysis assays: Hemolysis assays were conducted to evaluate the in vitro hemocompatibility of PBLT films. A 4% suspension of rat red blood cells was prepared and distributed into 1.5 mL centrifuge tubes, into which circular films measuring 6 mm in diameter were placed. The samples were incubated at 37 ℃ for 2 hours, followed by centrifugation at 5000 rpm for 10 minutes. The color and clarity of the supernatants were assessed visually, and aliquots were transferred to a 96-well plate for optical density (OD) measurement at 545 nm using a multifunctional microplate spectrophotometer (Thermo Fisher Scientific, USA). Hemolysis rates were calculated from these OD values to determine the hemocompatibility of the PBLT films. The experimental groups included: (1) positive control with 1% Triton X-100; (2) blank control with normal saline only; (3) PBL60T40; and (4) PBL60T40-0.9%.

2. Supplementary figures and tables.

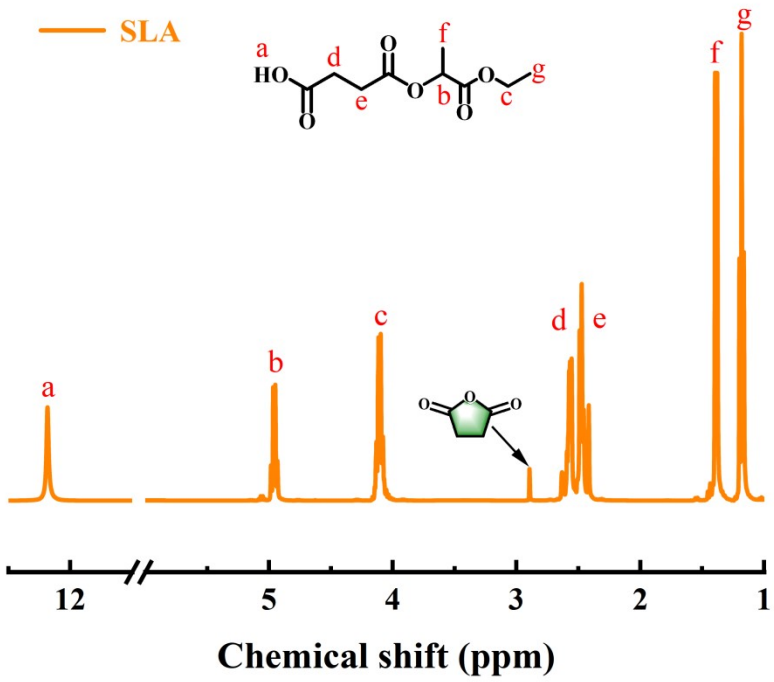

Figure S1. ^{1}H NMR Spectrum of SLA Monomer.

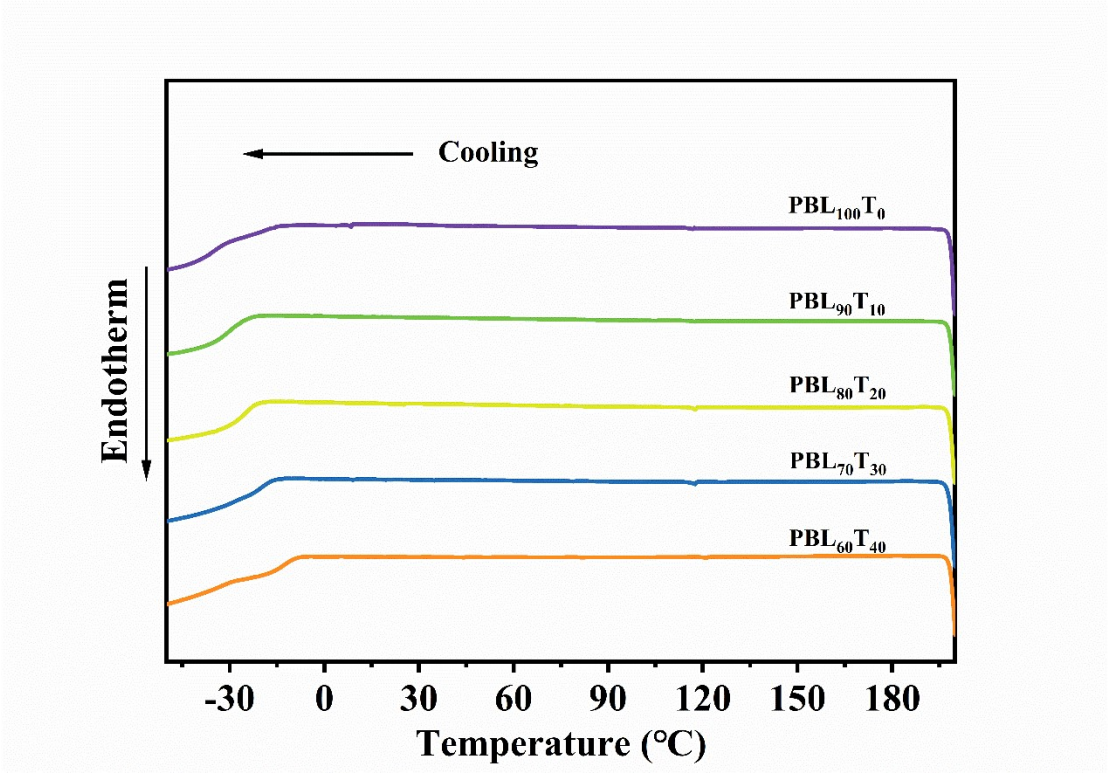

Figure S2. Cooling curves of PBLT copolyesters.

Table S1. Thermal properties of PBLT copolyesters.

Samples	Cooling scans		Second heating scans				
	T_c (°C)	ΔH_c (J/g)	T_{cc} (°C)	ΔH_{cc} (J/g)	T_m (°C)	ΔH_m (J/g)	T_g (°C)
$PBL_{60}T_{40}$	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	-10.4
$PBL_{70}T_{30}$	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	-16.6
$PBL_{80}T_{20}$	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	-22.3
$PBL_{90}T_{10}$	n.d.	n.d.	n.d.	n.d.	73.4	-2.6	-27.0
$PBL_{100}T_0$	n.d.	n.d.	26.5	20.7	78.5	-24.0	-29.9

Table S2. Mechanical Properties of PBLT copolyesters.

Sample	E (MPa)	σ_t (MPa)	ε_b (%)
$PBL_{60}T_{40}$	9.8±0.1	4.5±0.2	1808±93
$PBL_{70}T_{30}$	0.6±0.1	3.1±0.4	1395±25
$PBL_{80}T_{20}$	35.9±0.4	13.7±0.1	2241±55
$PBL_{90}T_{10}$	85.2±0.9	18.7±0.9	1715±84
$PBL_{100}T_0$	90.5±10.8	7.4±0.1	234±36

Table S3. Elastic properties of PBLT copolyesters at 200% strain.

Samples	R_r (1) (%)	R_r (2) (%)	R_r (3) (%)	R_r (4) (%)	R_r (5) (%)
$PBL_{60}T_{40}$	75.5 ± 0.4	94.4 ± 0.7	95.7 ± 0.6	98.0 ± 0.3	99.0 ± 0.2
$PBL_{70}T_{30}$	65.5 ± 0.6	93.7± 1.1	95.2 ± 0.5	97.5 ± 0.4	98.4 ± 0.1

Table S4. The mass of each monomer and the wt% of glycerol in the crosslinked products.

Sample	SLA (g)	DMT (g)	BDO (g)	TBT (g)	TPP (g)	glycerol (g)	glycerol (wt%)
$PBL_{60}T_{40}$-0.3%	37.488	21.148	35.248	0.136	0.131	0.267	0.283
$PBL_{60}T_{40}$-0.5%	37.488	21.148	35.248	0.136	0.131	0.445	0.471
$PBL_{60}T_{40}$-0.9%	37.488	21.148	35.248	0.136	0.131	0.802	0.849
$PBL_{70}T_{30}$-0.3%	43.736	15.862	35.248	0.136	0.131	0.267	0.280
$PBL_{70}T_{30}$-0.5%	43.736	15.862	35.248	0.136	0.131	0.445	0.467
$PBL_{70}T_{30}$-0.9%	43.736	15.862	35.248	0.136	0.131	0.802	0.841

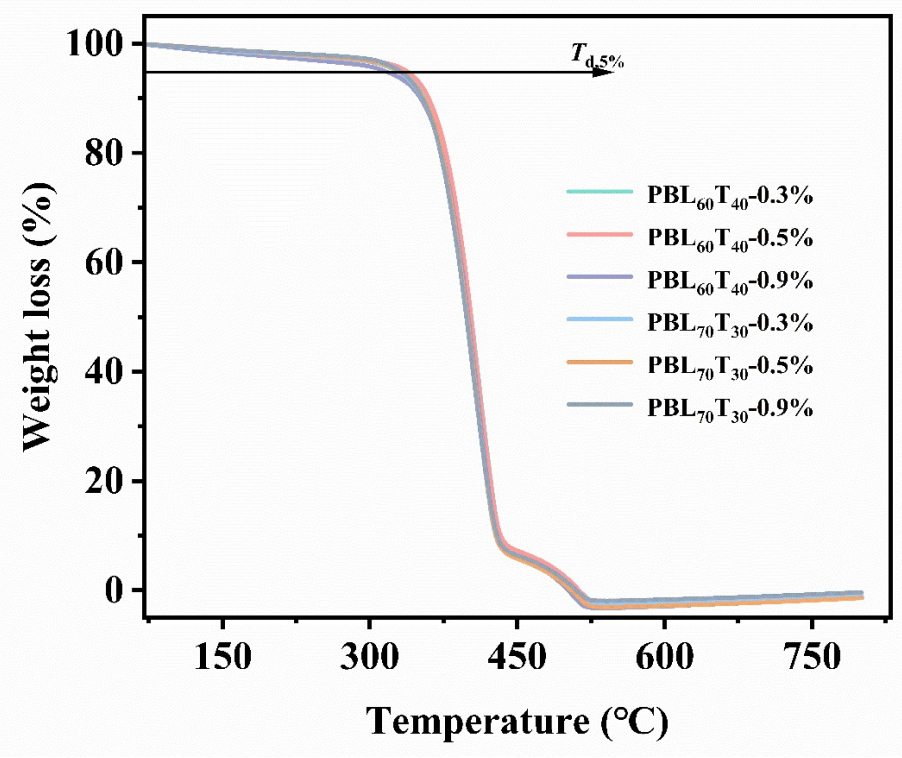

Figure S3. The TGA curve of the PBLT micro-crosslinked thermoplastic elastomer under air atmosphere

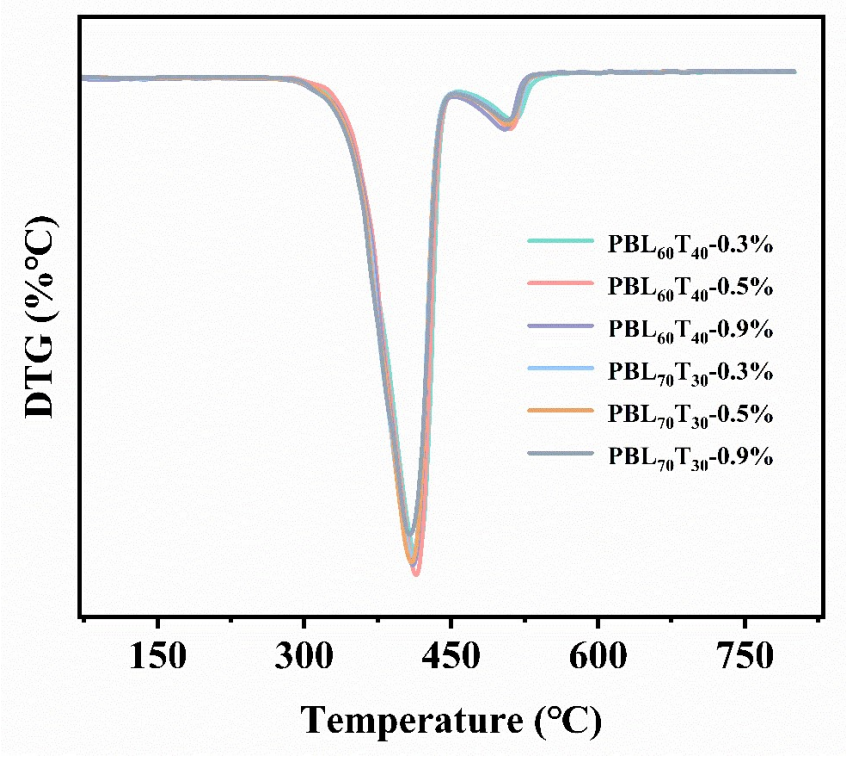

Figure S4. The DTG curve of the PBLT micro-crosslinked thermoplastic elastomer under air atmosphere

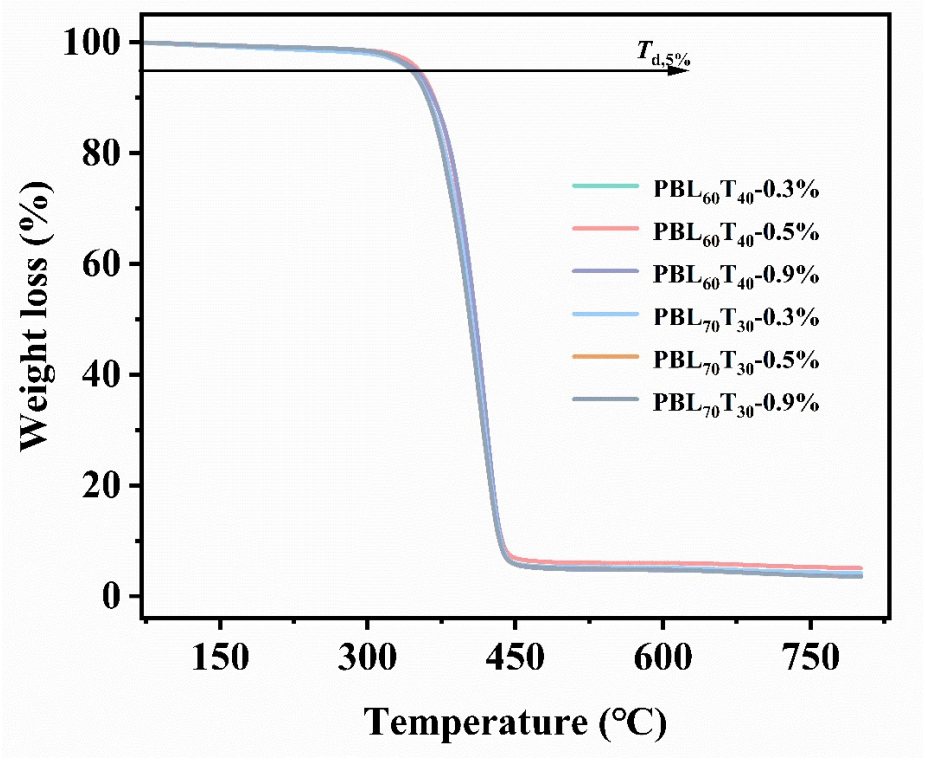

Figure S5. The TGA curve of the PBLT micro-crosslinked thermoplastic elastomer under N_2 atmosphere

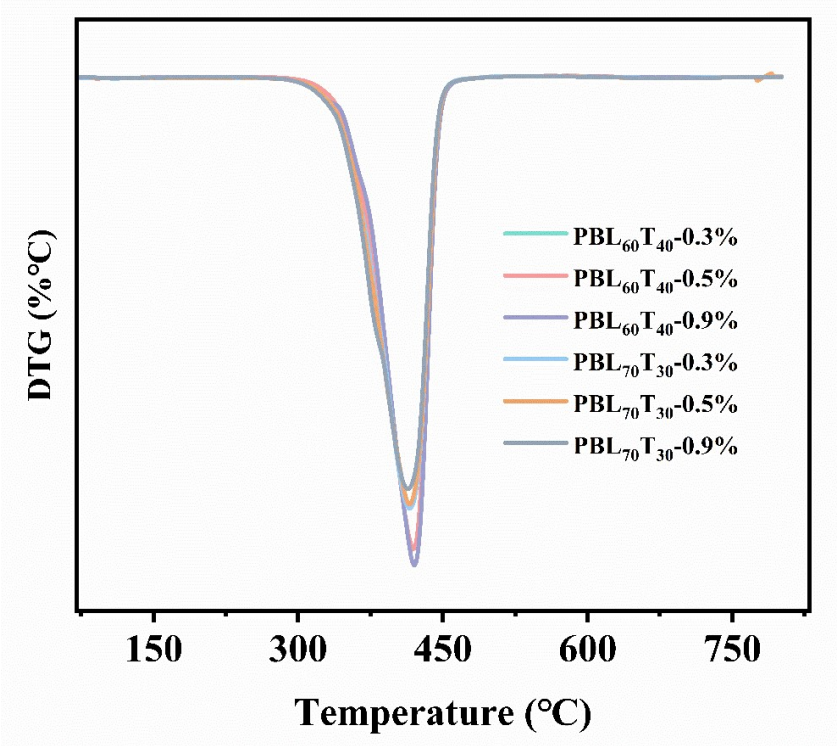

Figure S6. The DTG curve of the PBLT micro-crosslinked thermoplastic elastomer under N_2 atmosphere

Table S5. Elastic properties of PBLT micro-crosslinked elastomer at 200% strain.

Samples	R_r (1) (%)	R_r (2) (%)	R_r (3) (%)	R_r (4) (%)	R_r (5) (%)
$PBL_{60}T_{40}$-0.3%	59.7 ± 0.5	93.4 ± 0.8	95.4 ± 0.7	97.7 ± 0.5	98.5 ± 0.2
$PBL_{60}T_{40}$-0.5%	60.8 ± 0.7	92.5 ± 1.2	95.3 ± 0.6	97.5 ± 0.4	98.3 ± 0.3
$PBL_{60}T_{40}$-0.9%	58.6 ± 0.6	92.3 ± 0.7	94.7 ± 0.4	97.2 ± 0.5	98.4 ± 0.2
$PBL_{70}T_{30}$-0.3%	67.6 ± 0.8	93.9 ± 0.8	96.1 ± 0.5	98.2 ± 0.4	98.6 ± 0.1
$PBL_{70}T_{30}$-0.5%	61.9 ± 0.6	92.5 ± 0.7	94.8 ± 0.4	97.5 ± 0.6	98.3 ± 0.2
$PBL_{70}T_{30}$-0.9%	68.5 ± 0.8	93.7 ± 0.9	96.2 ± 0.5	98.1 ± 0.4	98.5 ± 0.1

Table S6. The properties comparation of $PBL_{60}T_{40}$-0.9% with representative TPEs.

Samples	E (MPa)	σ_t (MPa)	ε_b (%)	$R_{r\,(200\%)}$ (1) (%)	Reference
PBAC-80-cis	166 ± 8.0	25 ± 1.0	682 ± 23	50 ± 2.0	[1]
PBAC58	64 ± 4.0	14 ± 1.0	759 ± 8	30 ± 1.0	[2]
PBC36	99 ± 10.0	27 ± 1.0	880 ± 17	35 ± 1.0	[3]
PBC44	81 ± 12.0	28 ± 1.0	1360 ± 28	41 ± 2.0	[3]
PBC71	111 ± 12.0	18 ± 1.0	1230 ± 35	64 ± 4.0	[3]
PNF-70PTMG	43 ± 1.0	22 ± 2.0	1042 ± 51	80.1 ± 1.4	[4]
PCF-70PTMG	35 ± 4.0	22 ± 3.0	697 ± 40	76.5 ± 1.0	[5]
PBT-60PTMG	48 ± 2.0	14 ± 1.5	1420 ± 20	73.1 ± 1.2	[6]
PTT-70PTMG	35 ± 7.0	17 ± 2.0	832	72.5 ± 2.5	[7]
$PBL_{60}T_{40}$-0.9%	21.3±1.1	16.1±0.3	2016±62	58.6 ± 0.6	this work

References

1 F. Liu, J. Qiu, J. Wang, J. Zhang, H. Na and J. Zhu, *RSC Adv.*, 2016, **6**, 65889–65897.

2 J. Qiu, F. Liu, J. Zhang, J. Chen, H. Na and J. Zhu, *Polymer Engineering & Sci*, 2017, **57**, 1277–1284.

3 F. Liu, J. Zhang, J. Wang, X. Liu, R. Zhang, G. Hu, H. Na and J. Zhu, *J. Mater. Chem. A*, 2015, **3**, 13637–13641.

4 T. Yang, F. Liu, R. Gao, J. Li, J. Wang and J. Zhu, *European Polymer Journal*, 2023, **198**, 112385.

5 J. Wang, X. Zhang, X. Fei, R. Gao, F. Liu, L. Fan, J. Zhu and X. Liu, *ACS Sustainable Chem. Eng.*, 2022, **10**, 13595–13606.

6 H. Xie, H. Lu, Z. Zhang, X. Li, X. Yang and Y. Tu, *Macromolecules*, 2021, **54**, 2703–2710.

7 A. Szymczyk, J. Nastalczyk, R. J. Sablong and Z. Roslaniec, *Polymers for Advanced Techs*, 2011, **22**, 72–83.