

Sustainable and Fast Degradable Poly(butylene carbonate-co-cyclohexanedicarboxylate): Influence of Composition on Crystallization, Mechanical and Barrier Properties

Han Hu, ^{a,b} Ruoyu Zhang, ^{a*} Wu Bin Ying, ^a Lei Shi, ^a Chenkai Yao, ^a Zhengyang Kong, ^a Kai Wang, ^a
Jinggang Wang, ^a Jin Zhu ^{a*}

Contents:

Total number of pages: 6

Total number of Figures: 4

Total number of Tables: 6

S1. ¹³C-NMR Spectra.

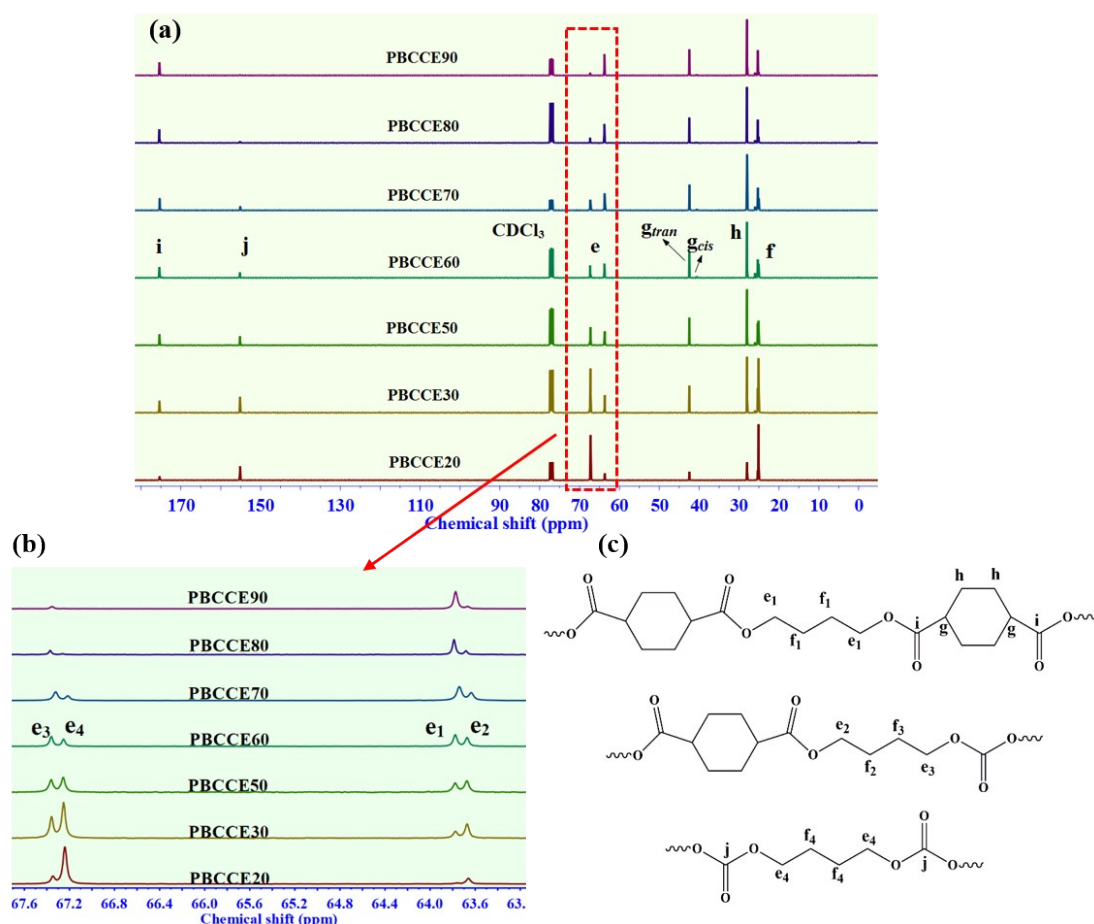


Fig. S1 (a) ¹³C NMR spectra of the PBCCEs. (b) The larger image of spectra between 63 and 68 ppm. (c)

Three triads for PBCCE.

S2. Thermal Properties Tested from DSC.

Table S1. Thermal properties of PBCCEs.

Sample	1st heating scan		Cooling scan		2nd heating scan				
	T_m (°C)	ΔH_m (J/g)	T_c (°C)	ΔH_c (J/g)	T_g (°C)	T_{cc} (°C)	ΔH_{cc} (J/g)	T_m (°C)	ΔH_m (J/g)
PBC	59.8	43.3	nd	nd	-32.3	nd	nd	55.9	0.9
PBCCE20	48.4	29.0	nd	nd	-26.5	nd	nd	nd	nd
PBCCE30	55.2	8.5	nd	nd	-18.5	nd	nd	nd	nd
PBCCE50	64.0	13.9	nd	nd	-13.2	nd	nd	nd	nd
PBCCE60	89.2(43.8)	10.4(2.9)	nd	nd	-11.4	49.7	10.7	88.3	10.7
PBCCE70	112.6(47.0)	12.6(1.8)	60.7	21.7	-7.0	nd	nd	109.5	15.0
PBCCE80	139.8(48.8)	17.0(1.2)	105.4	28.1	-1.4	nd	nd	137.9	19.0
PBCCE90	153.5(48.5)	19.0(1.0)	119.5	28.8	5.1	nd	nd	150.8	20.5
PBCE	158.9(52.7)	23.6(1.0)	123.9	31.5	7.9	nd	nd	156.8	25.0

S3. Fitting of Fox Equation.

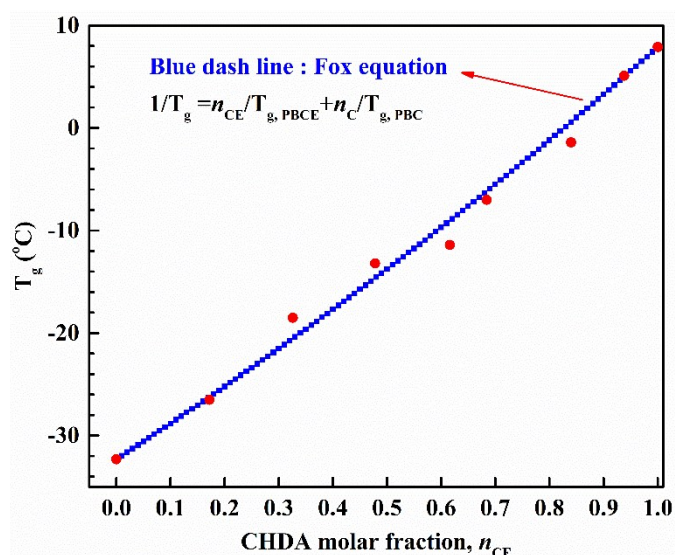


Fig. S2 Composition-dependence of T_g in PBCCEs as a function of CHDA molar fraction. The blue dash line was the results calculated from Fox equation by using T_g of PBC and PBCE.

S4. Isothermal Crystallization Behavior

Table S2. Isothermal Crystallization Kinetics Parameters of PBCE, PBCCE90 and PBCCE70.

Sample	T_c (°C)	n	k (min ⁻ⁿ)	$t_{1/2}$ (min)	$1/t_{1/2}$ (min ⁻¹)
PBCCE70	45	2.2	3.1	0.501	2.0
	50	2.3	3.3	0.498	2.0
	55	2.3	2.4	0.585	1.7
	60	2.4	1.4	0.736	1.4
	65	2.5	8.9×10^{-1}	0.905	1.1
	70	2.6	3.6×10^{-1}	1.29	7.7×10^{-1}

PBCCE90	100	2.9	52.4	0.227	4.4
	105	2.8	35.1	0.243	4.1
	110	2.8	58.4	0.203	4.9
	115	2.4	21.1	0.247	4.0
	120	2.7	11.8	0.354	2.8
	125	2.8	1.75	0.722	1.4
PBCE	105	3.1	30.9	0.294	3.4
	110	3.1	53.8	0.246	4.1
	115	2.6	28.5	0.238	4.2
	120	2.5	30.9	0.219	4.6
	125	2.7	11.5	0.347	2.9
	130	3.0	0.17	1.58	$6.3 \cdot 10^{-1}$

S5. Heating Scans after Isothermal Crystallization.

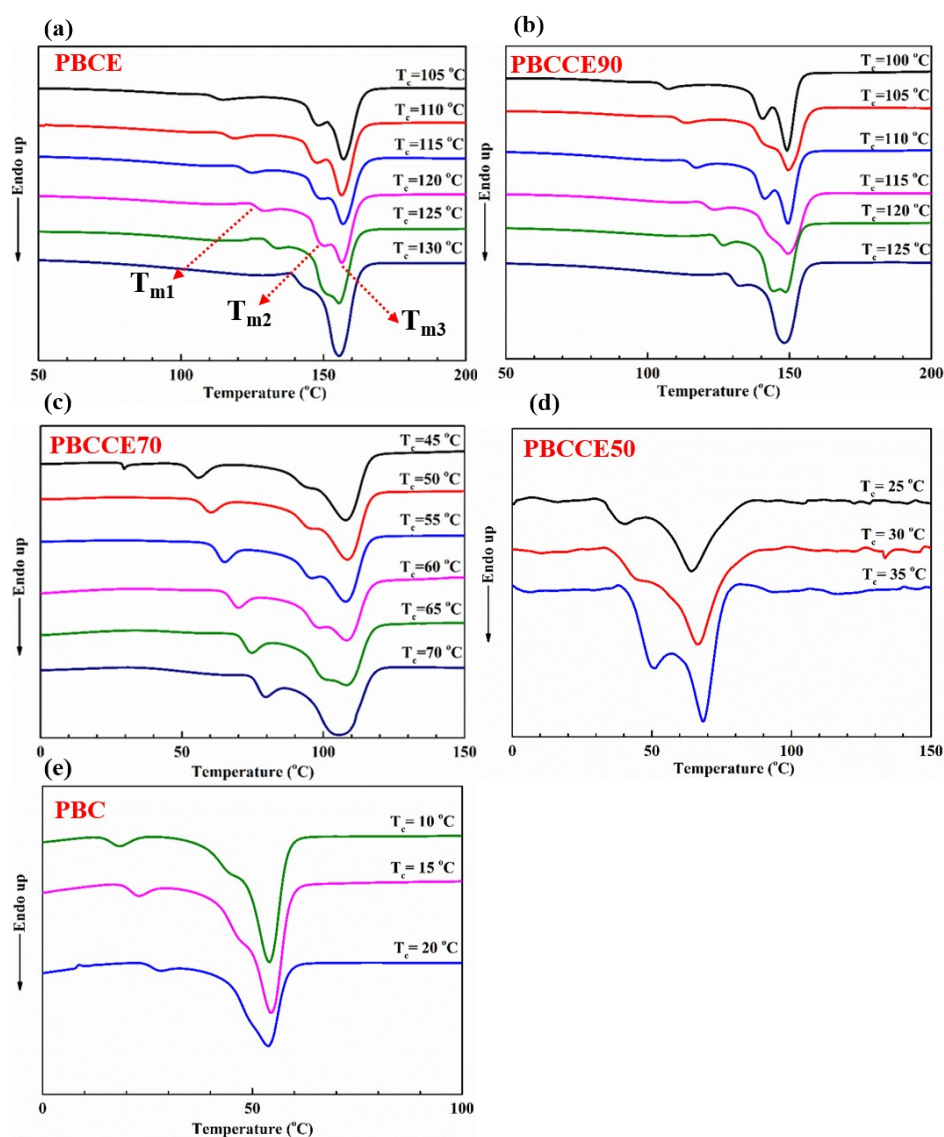


Fig. S3 Melting behaviors of PBCE (a), PBCCE90 (b), PBCCE70 (c), PBCCE50 (d) and PBC (e) after

isothermally crystallized at various T_c .

S6. Thermal Stability.

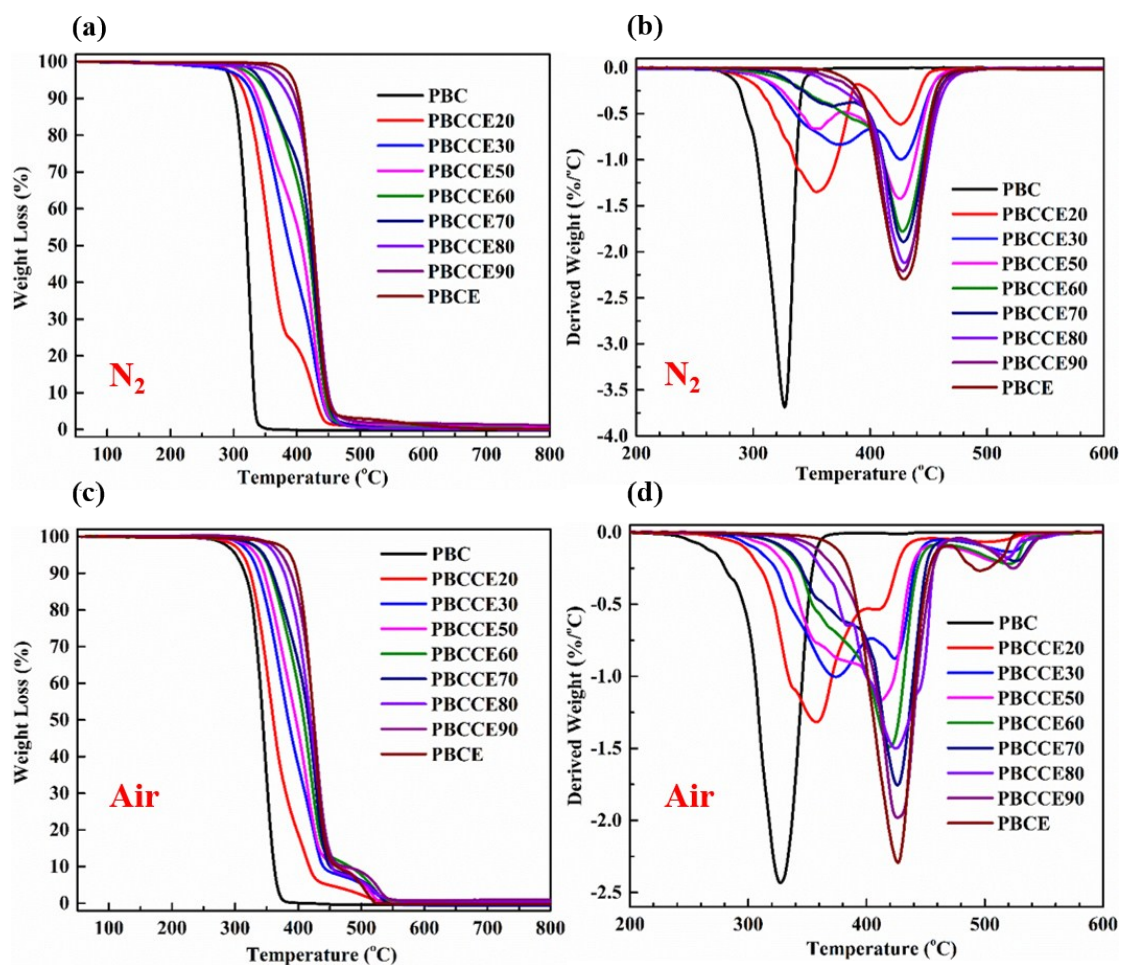


Fig. S4 TGA (a) and DTG (b) traces of PBCCEs at a heating rate of $20\text{ }^{\circ}\text{C min}^{-1}$.

Table S3. Thermal stability of PNSFs under N_2 and air.

Sample	N_2		Air	
	$T_{5\%}$ ($^{\circ}\text{C}$)	$T_{d,\max}$ ($^{\circ}\text{C}$)	$T_{5\%}$ ($^{\circ}\text{C}$)	$T_{d,\max}$ ($^{\circ}\text{C}$)
PBC	295	312	301	327
PBCCE20	307	355,426	312	358,411
PBCCE30	316	374,426	324	374,423
PBCCE50	325	356,426	334	375,414
PBCCE60	336	428	344	421
PBCCE70	343	429	346	427
PBCCE80	370	430	364	424
PBCCE90	383	428	374	426
PBCE	394	429	387	427

S7. Mechanical Properties.

Table S4. Elastic modulus (E), tensile strength (σ_b) and elongation at break (ϵ_b) of PBCCEs and PBAT.

Sample	E (MPa)	σ_b (MPa)	ϵ_b (%)
PBC	330±14	42.9±0.5	495±10
PBCCE30	3±1	0.5±0.1	808±5
PBCCE50	87±3	22.8±0.4	930±23
PBCCE60	133±2	30.5±1.8	791±15
PBCCE70	200±4	27.8±0.3	565±13
PBCCE80	390±23	37.8±0.8	461±12
PBCCE90	520±18	39.5±2.1	413±14
PBCE	772±15	34.9±1.2	31±5
PBAT	85±1	17.7±0.2	743±4

S8. Barrier Properties Compared with PBAT.

Table S5. CO₂, O₂ and H₂O barrier properties of PBCCEs, compared with PBAT.

Sample	CO ₂	BIF _p	O ₂	BIF _p	H ₂ O	BIF _p
PBAT	5.9	1	0.76	1	3.52 *10 ⁻¹³	1
PBCCE50	2.0	3.0	0.55	1.4	3.14 *10 ⁻¹³	1.2
PBCCE60	0.60	9.8	0.29	2.6	1.83 *10 ⁻¹³	1.9
PBCCE70	0.52	11.3	0.25	3.0	1.36 *10 ⁻¹³	2.6
PBCCE80	0.31	19.0	0.21	3.6	1.04 *10 ⁻¹³	3.4
PBCCE90	0.23	25.0	0.062	12.3	7.51 *10 ⁻¹⁴	4.7
PBCE	0.21	28.0	0.050	15.2	6.88 *10 ⁻¹⁴	5.1

S9. Molecular Weights of PBCCEs after Enzymatic Degradation.

Table S6. Molecular weights of PBCCEs after enzymatic degradation of 30 days.

Sample	Before enzymatic degradation			After enzymatic degradation		
	M _n (g/mol)	M _w (g/mol)	DI	M _n (g/mol)	M _w (g/mol)	DI
PBC	4.09×10 ⁴	7.75×10 ⁴	1.9	2.33×10 ⁴	4.66×10 ⁴	2.0
PBCCE20	5.61×10 ⁴	9.36×10 ⁴	1.7	3.34×10 ⁴	6.02×10 ⁴	1.8
PBCCE30	6.13×10 ⁴	9.66×10 ⁴	1.6	4.72×10 ⁴	7.55×10 ⁴	1.6
PBCCE50	5.58×10 ⁴	9.44×10 ⁴	1.7	1.56×10 ⁴	2.81×10 ⁴	1.8
PBCCE60	5.33×10 ⁴	8.53×10 ⁴	1.6	4.31×10 ⁴	6.89×10 ⁴	1.6
PBCCE70	4.53×10 ⁴	7.44×10 ⁴	1.6	4.41×10 ⁴	7.05×10 ⁴	1.6