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Novel biobased, flexible blocky copolyesters based on poly(lactic acid) and poly(ethylene azelate)

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Supplementary information

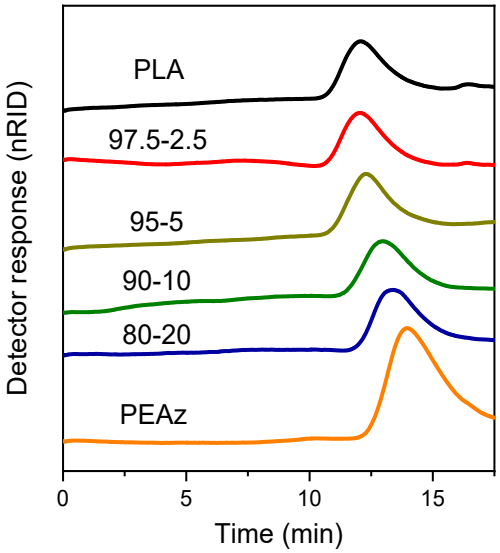


Figure S1. GPC curves of PLA, PEAz and PLA-b-PEAz copolyester.

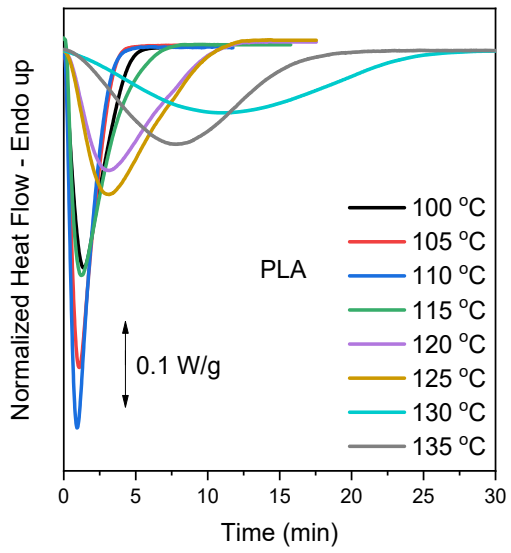
Table S1. Composition of the copolyesters.

PLA-PEAz copolyesters	PEAz in the premix (wt %)	PEAz in the premix (g)	PEAz in the premix (mmol)[1]	LA in the premix (g)	LA in the premix (mol)[2]	PEAz in the premix (mol %)	PEAz by NMR (mol%)
97.5-2.5	2.5	2.5	11.7	97.5	0.68	1.7	2.2[3]
95-5	5	5	23.3	95	0.66	3.4	4.4[3]
90-10	10	10	46.6	90	0.62	6.9	9.4
80-20	20	20	93.2	80	0.56	14.4	18.8

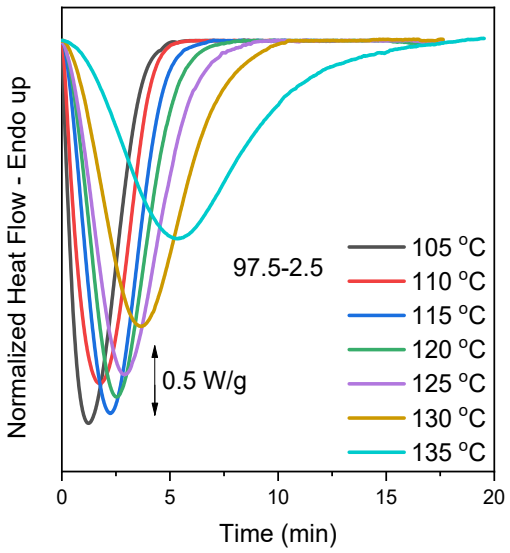
[1]: Calculated using the molecular weight of the repeating unit of PEAz.

[2]: Calculated using the molecular weight of lactide.

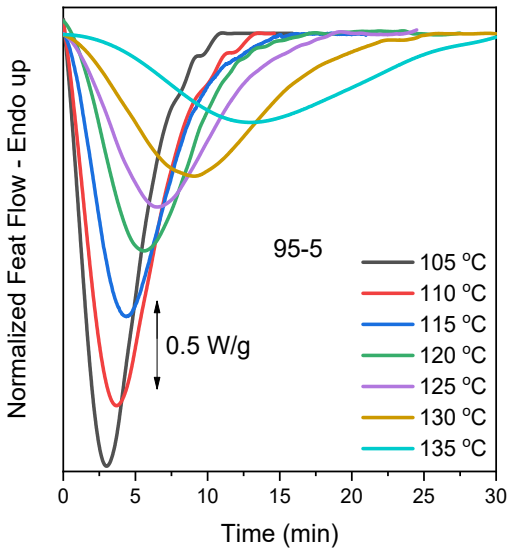
[3]: Indicative as below the limit of quantification of NMR.


Normalized Heat Flow - Endo up
PLA
0.1 W/g
100 °C
105 °C
110 °C
115 °C
120 °C
125 °C
130 °C
135 °C
0 5 10 15 20 25 30
Time (min)

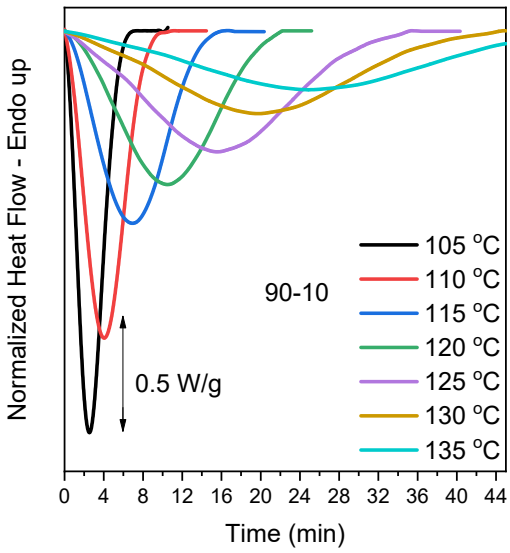
(**a**)


Normalized Heat Flow - Endo up
97.5-2.5
0.5 W/g
105 °C
110 °C
115 °C
120 °C
125 °C
130 °C
135 °C
0 5 10 15 20
Time (min)

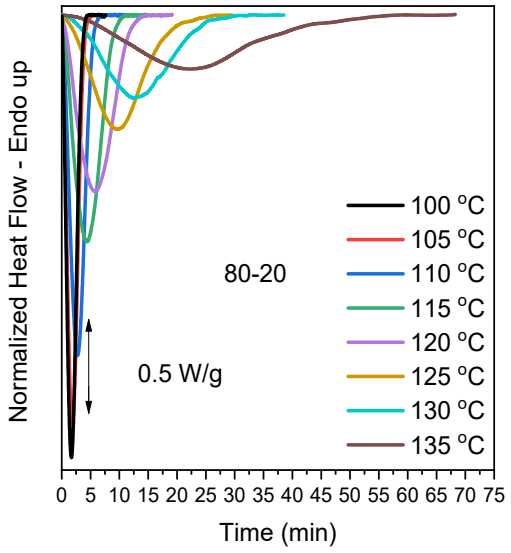
(**b**)


Normalized Feat Flow - Endo up
95-5
0.5 W/g
105 °C
110 °C
115 °C
120 °C
125 °C
130 °C
135 °C
0 5 10 15 20 25 30
Time (min)

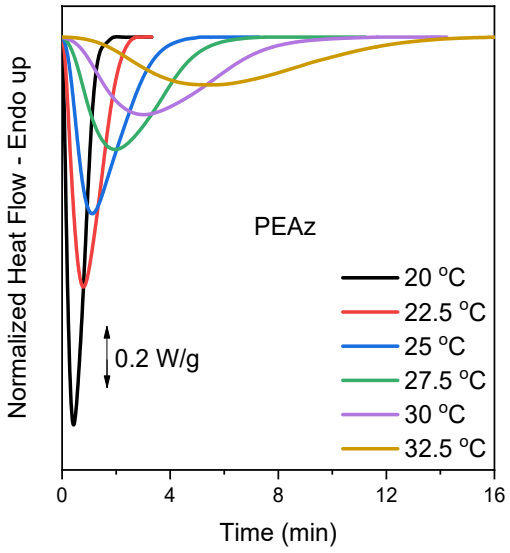
(**c**)


Normalized Heat Flow - Endo up
90-10
0.5 W/g
105 °C
110 °C
115 °C
120 °C
125 °C
130 °C
135 °C
0 4 8 12 16 20 24 28 32 36 40 44
Time (min)

(**d**)


Normalized Heat Flow - Endo up
80-20
0.5 W/g
100 °C
105 °C
110 °C
115 °C
120 °C
125 °C
130 °C
135 °C
0 5 10 15 20 25 30 35 40 45 50 55 60 65 70 75
Time (min)

(**e**)


Normalized Heat Flow - Endo up
PEAz
0.2 W/g
20 °C
22.5 °C
25 °C
27.5 °C
30 °C
32.5 °C
0 4 8 12 16
Time (min)

(**f**)

Figure S2. Crystallization exothermic peaks during isothermal melt crystallization at the corresponding temperatures of (**a**) PLA, PLA-b-PEAz copolyesters, (**b**), 97.5-2.5, (**c**) 95-5, (**d**) 90-10, (**e**) 80-20, and (**f**) PEAz.

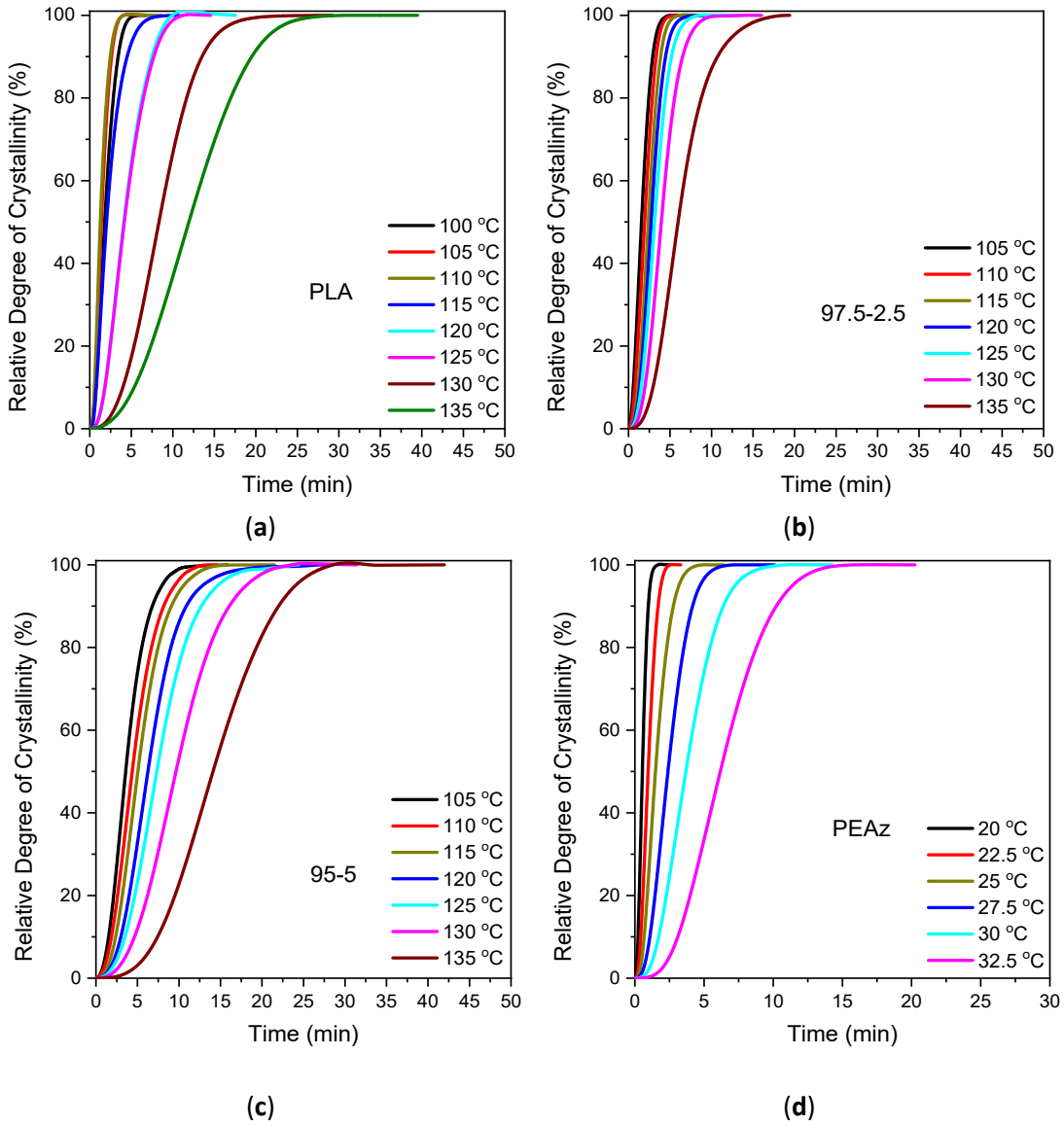
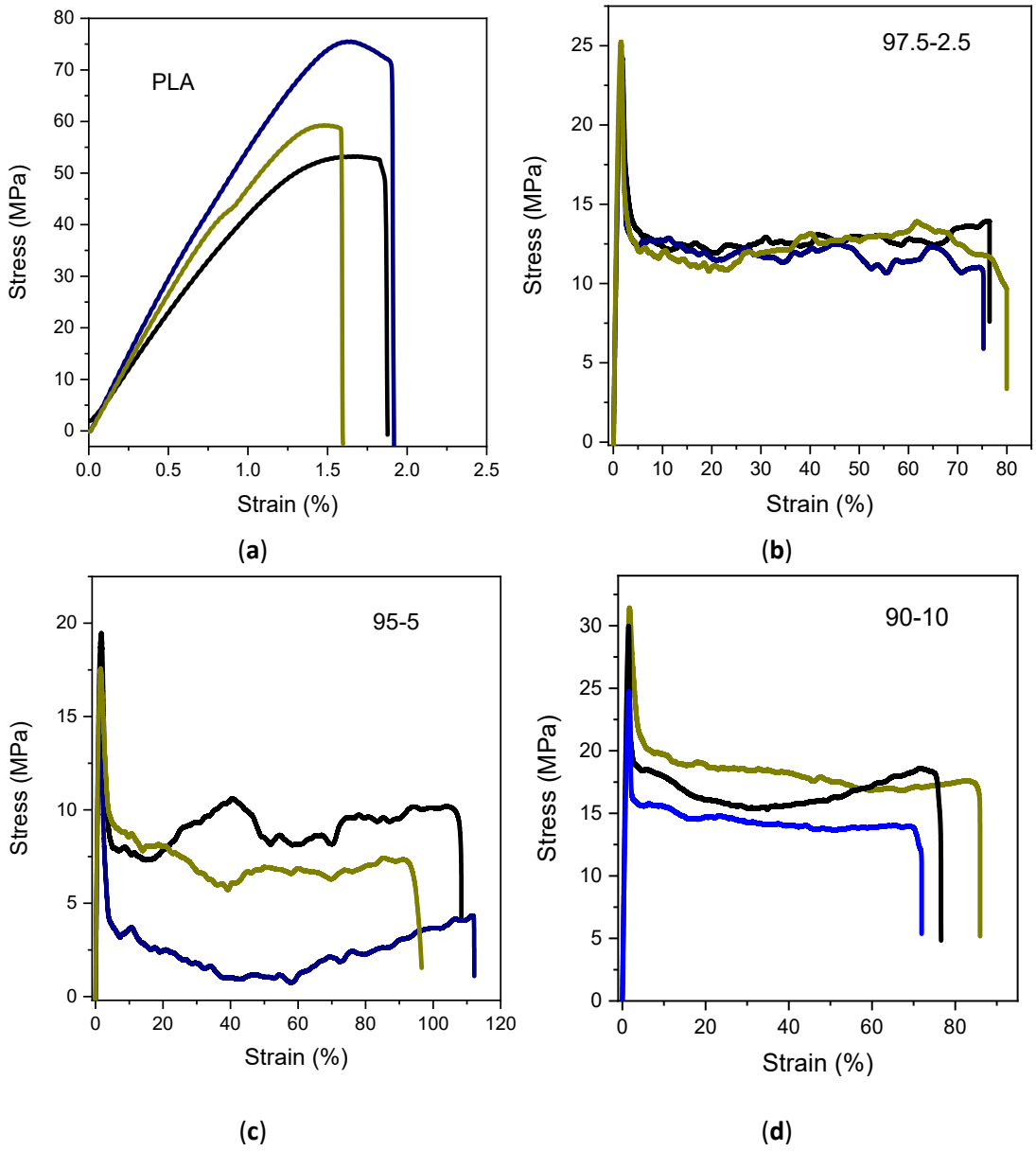


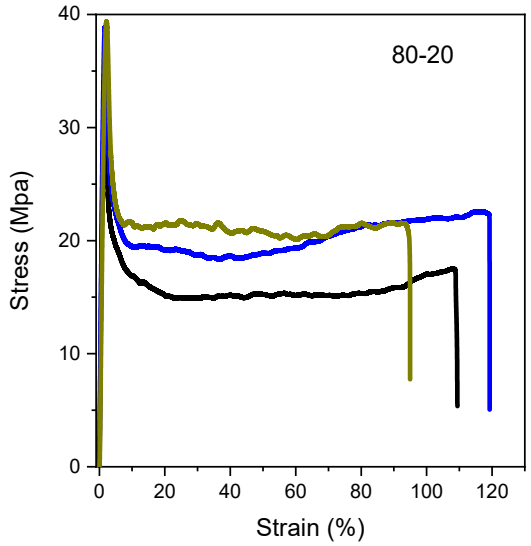
Figure S3: Relative degree of crystallinity as a function of time of (**a**) PLA, PLA-b-PEAz copolyesters **(b)** 97.5-2.5, (**c**) 95-5 and (**d**) PEAz at various isothermal melt crystallization temperatures.

PLA-b-PEAz copolyesters	T_{onset} (°C)	$T_{DTG, max}$ (°C)	T_{end} (°C)	Mass loss temperature range (°C)	Mass loss (%)	Residual (%)
PLA	348/-	380/-	393/-	270-410/-	95.92/-	0.96
97.5-2.5	355/-	385/-	399/-	290-430/-	94.73/-	1.18
95-5	334/-	385/430	403/-	270-430/ 430-470	90.79/2.1	1.13
90-10	337/438	381/443	398/458	270-430/ 430-470	89.65/4.5	1.68
80-20	318/443	371/452	399/471	270-430/ 430-500	82.62/13.11	2.12
PEAz	-/454	-/466	-/467	-/400-520	-/94.59	2.31

Table S2. Thermal degradation data of PLA, PEAz and their copolymers.

*The values before end after the symbol '/'are corresponding to the first and the second degradation step.



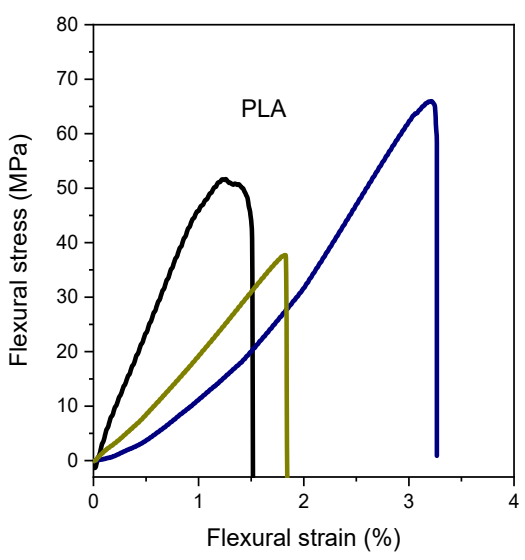


(**e**)

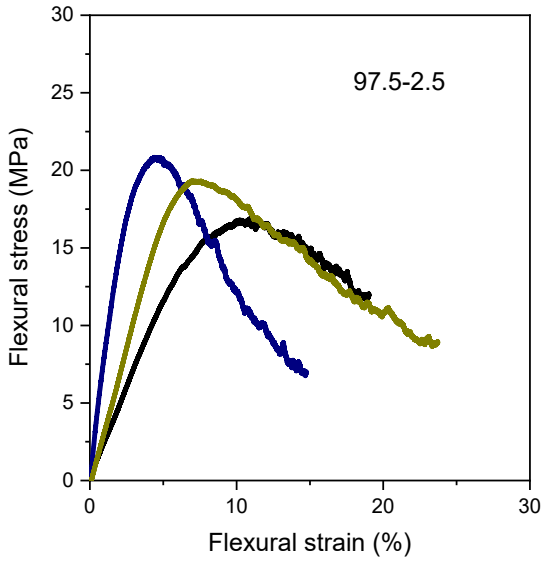
Figure S4. Tensile stress – strain curves of PLA and PLA-b-PEAz copolyesters.

Table S3. Tensile data of PLA and PLA-b-PEAz copolyesters.

Sample	Tensile Stress at Break (MPa)	Tensile Stress at Yield (MPa)	Elongation (%)	Young's Modulus E (MPa)
PLA	57.2 ± 9.7	-	1.8 ± 0.5	5412.9 ± 815.3
PLA-PEAz_97.5-2.5	11.2 ± 2.0	21.9 ± 1.2	78.2 ± 4.0	2150.1 ± 103.1
PLA-PEAz_95-5	6.1 ± 1.8	15.8 ± 1.5	106.0 ± 7.6	1798.6 ± 150.7
PLA-PEAz_90-10	16.6 ± 2.3	28.7 ± 3.5	78.1 ± 7.1	2285.7 ± 320.2
PLA-PEAz_80-20	20.4 ± 2.6	36.9 ± 3.9	107.8 ± 12.2	2911.9 ± 292.5



(**a**)



(**b**)

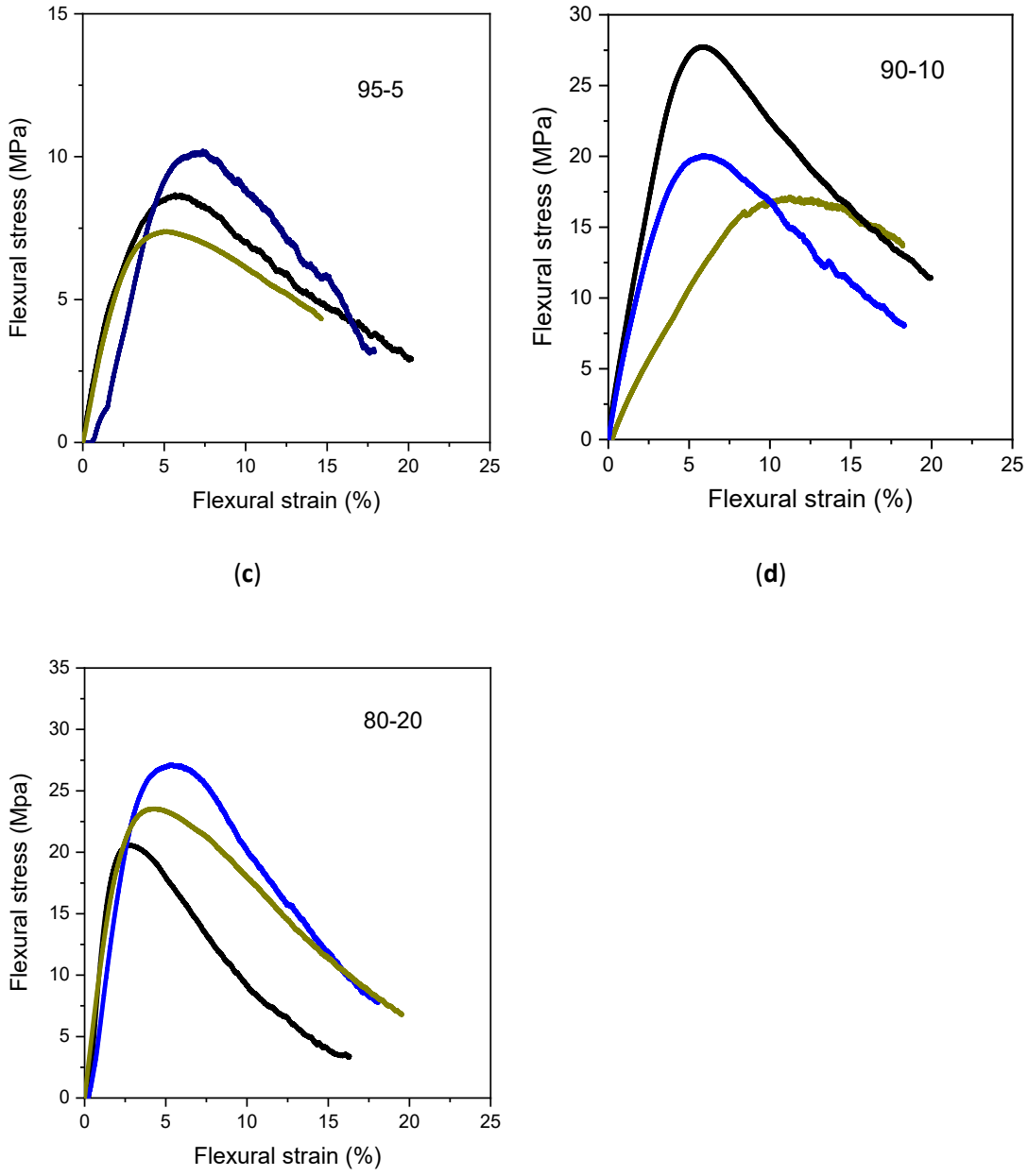


Figure S5. 3-point bend curves of PLA and PLA-b-PEAz copolyesters.

Table S4. Flexural data of PLA and PLA-b-PEAz copolyesters.

Sample	Flexural strength (MPa)	Flexural Modulus (MPa)
PLA	51.5 ± 14.1	1507.6 ± 152.0
PLA-PEAz_97.5-2.5	18.9 ± 2.1	474.6 ± 259.0
PLA-PEAz_95-5	8.7 ± 1.5	206.2 ± 27.8
PLA-PEAz_90-10	21.5 ± 5.7	586.0 ± 296.8
PLA-PEAz_80-20	23.5 ± 3.3	730.6 ± 123.4