Supporting information

Blending with poly(L-lactic acid) improves the printability of poly(L-lactide-co-caprolactone) and enhances the potential application in cartilage tissue engineering

Ruiping Duan[1,#], Yimeng Wang[1,#], Yiyun Zhang[1,#], Ziqiang Wang[1,#], Fuchong Du[1], Bo Du[1], Danning Su[1], Lingrong Liu[1], Xuemin Li[1,*], Qiqing Zhang[1,2,*]

[1] The Key Laboratory of Biomedical Material of Tianjin, Biomedical Barriers Research Center, Chinese Academy of Medical Sciences & Peking Union Medical College Institute of Biomedical Engineering, Tianjin 300192, P.R. China

[2] Institute of Biomedical Engineering, the Second Clinical Medical College, Jinan University (Shenzhen People's Hospital), Shenzhen 518020, Guangdong, P.R. China

[#] These authors contributed equally.

[*] Corresponding author: lixuemin-7205@vip.sina.com and zhangqiq@126.com

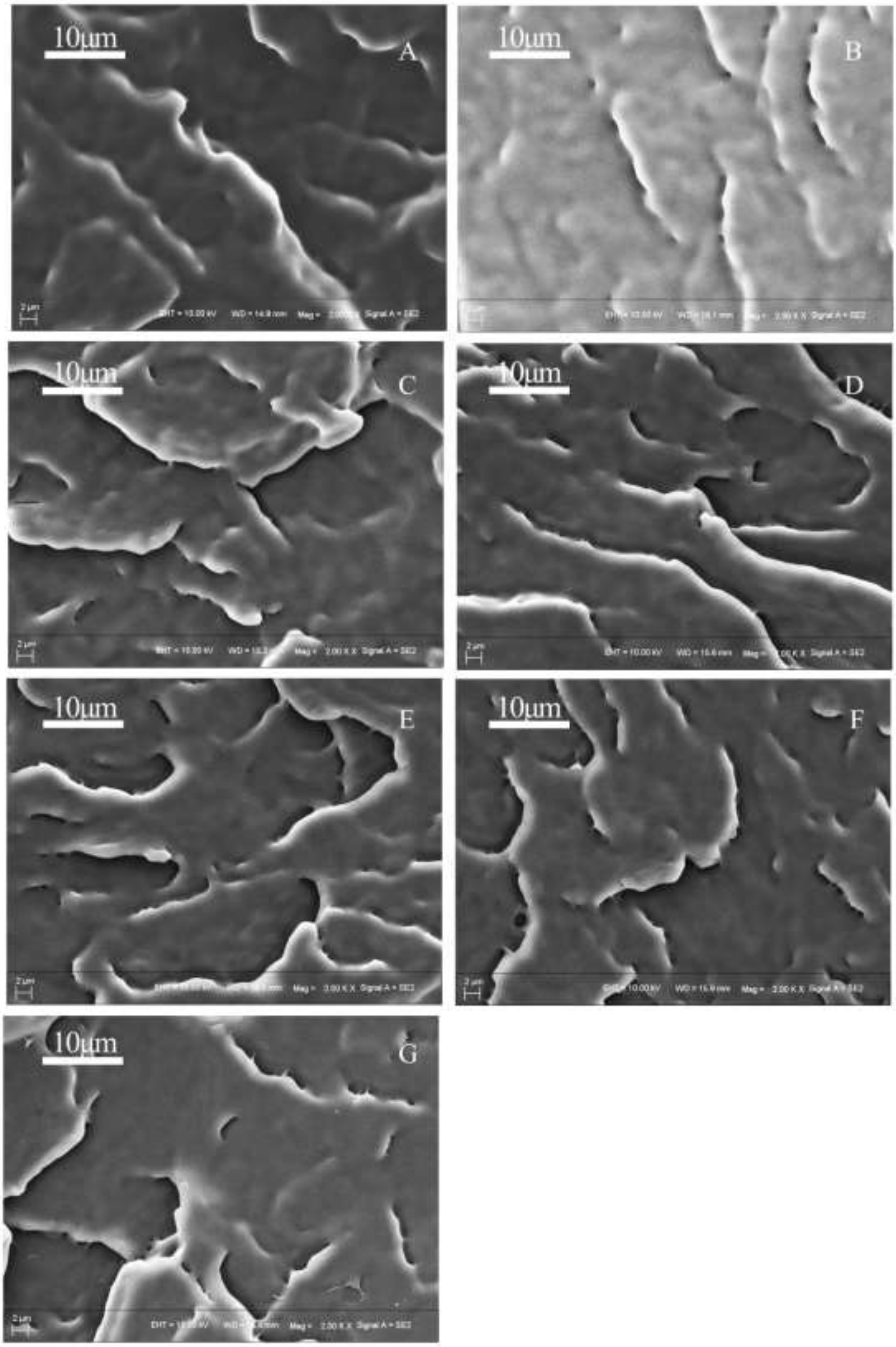

Figure S1. SEM images of the surfaces of the embrittled-broken samples. A, PLCL; B-G, PLCL/PLLA blends at different ratios; B, 10%PLLA; C, 20%PLLA; D, 30%PLLA; E, 40%PLLA; F, 50%PLLA; G, PLLA.

As shown in Figure S1, they were the SEM micrographs with high magnifications of cryo-fractured surfaces of PLCL/PLLA blends, corresponding to the Figure 4 in article.

Table S1. The difference in tensile properties of PLCL/PLLA blends.

Group		*P*		
		E	σ_{max}	ε_u
PLCL	PLCL90PLLA10	0.0208	0.0013	0.0021
	PLCL80PLLA20	0.0062	0.0019	0.0020
	PLCL70PLLA30	<0.0001	0.0125	0.0018
	PLCL60PLLA40	<0.0001	0.2032	0.0006
	PLCL50PLLA50	<0.0001	0.9413	<0.0001
	PLLA	<0.0001	0.0008	<0.0001
PLCL90PLLA10	PLCL80PLLA20	0.2374	0.9134	0.3449
	PLCL70PLLA30	<0.0001	0.5446	0.1576
	PLCL60PLLA40	<0.0001	0.1082	0.0201
	PLCL50PLLA50	<0.0001	0.0072	<0.0001
	PLLA	<0.0001	0.0104	<0.0001
PLCL80PLLA20	PLCL70PLLA30	<0.0001	0.518	0.5301
	PLCL60PLLA40	<0.0001	0.1084	0.1194
	PLCL50PLLA50	<0.0001	0.0082	0.0005
	PLLA	<0.0001	0.0124	<0.0001
PLCL70PLLA30	PLCL60PLLA40	0.0004	0.2689	0.3777
	PLCL50PLLA50	<0.0001	0.0284	0.0035
	PLLLA	<0.0001	0.0102	<0.0001
PLCL60PLLA40	PLCL50PLLA50	0.0022	0.2465	0.007
	PLLA	<0.0001	0.0053	<0.0001
PLCL50PLLA50	PLLA	<0.0001	0.0013	<0.0001

Note: E, elastic modulus; σ_{max}, tensile strength; ε_u, the ultimate strain or elongation at break.

As shown in Table S1, all data were expressed as the mean ± standard deviation (SD). Unpaired T test was performed to assess the statistical significance of differences between groups. The results of statistical analyses were performed using GraphPad Prism (version 7, GraphPad software Inc., San Diego, CA, USA) software based on statistically independent observations, and differences were considered statistically significant when the p-value was less than 0.05.

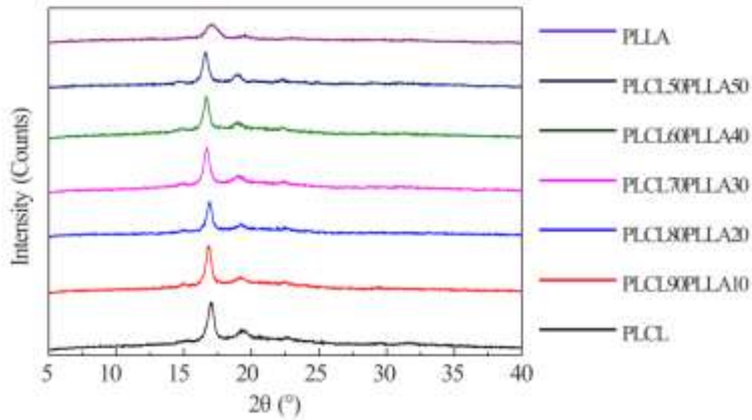

Figure S2. X-ray diffraction patterns of the filaments of PLCL/PLLA blends

In order to exploit the crystalline types of the samples, a wide-angle X-ray diffraction (XRD, Rigaku UItima IV) was performed by using an angle range 2θ=5-40° at 40 kV and 40mA. XRD patterns of the samples were obtained and showed in Figure S2. From the XRD spectra (Figure S2), it could be seen there were two main diffraction peaks at 2θ angles of 17.0 and 19.4 ° for all PLCL/PLLA blends. This result indicated that the crystallinity in blends do not vary substantially, which was consistent with the DSC results.

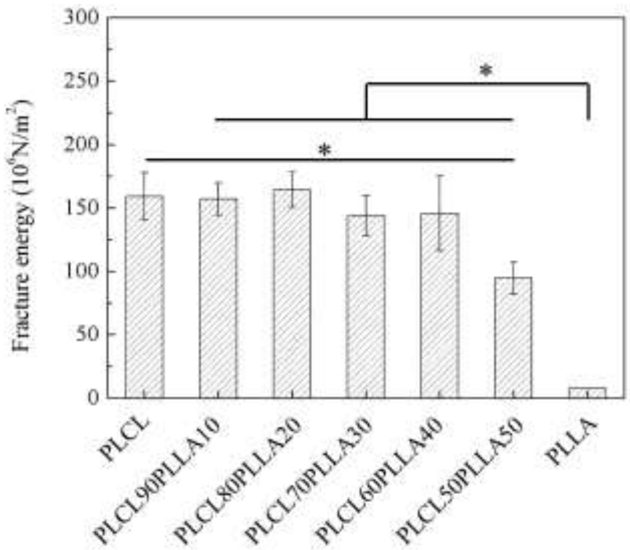

Figure S3. The area below stress-strain curves of PLCL/PLLA blends at different mass ratios.

The area below stress-strain curves was calculated to evaluate the fracture energy of blends based on Figure 5B, and the results showed in Figure S3. The results displayed there was no significant difference of the fracture energy between PLCL and the blends except PLCL50PLLA50, while a significant difference existed between PLLA and the blends. Therefore, the toughness of PLCL was well preserved after blending with PLLA, while the rigidity and stiffness of PLCL was increased.

Table S2. Mechanical properties of the 3D-printed scaffolds of PLCL/PLLA blends with different filling rate.

Infill ratio(%)	Scaffolds	E(MPa)	σ_{max}(MPa)	$t_{1/2}$(s)
40%	PLCL	0.52±0.07	0.07±0.003	110.62±8.24
	PLCL90PLLA10	34.03±5.06	3.34±0.53	10.36±2.91
	PLCL80PLLA20	45.45±2.46	5.06±0.92	17.17±0.61
	PLCL70PLLA30	42.26±1.24	5.76±0.69	16.64±2.03
	PLCL60PLLA40	49.37±7.42	5.50±2.00	20.48±5.04
	PLCL50PLLA50	53.84±12.73	7.00±2.16	41.32±0.74
	PLLA	68.84±12.31	3.77±1.31	—
50%	PLCL	0.76±0.04	0.12±0.009	155.13±7.60
	PLCL90PLLA10	42.45±0.29	5.27±1.40	11.12±2.41
	PLCL80PLLA20	51.88±4.81	5.82±0.47	17.77±2.43
	PLCL70PLLA30	56.19±8.95	6.12±2.00	23.97±9.94
	PLCL60PLLA40	56.73±5.44	6.00±1.99	32.79±5.20
	PLCL50PLLA50	67.35±8.16	7.49±1.39	48.94±15.76
	PLLA	134.69±7.70	17.87±1.28	341.64±10.13
60%	PLCL	0.96±0.05	0.15±0.005	177.93±15.77
	PLCL90PLLA10	54.82±1.84	5.51±0.88	16.00±1.73
	PLCL80PLLA20	56.74±5.08	6.24±0.52	19.23±1.65
	PLCL70PLLA30	63.81±4.50	6.64±0.49	21.27±1.15
	PLCL60PLLA40	70.58±6.70	8.04±0.89	36.08±4.17
	PLCL50PLLA50	81.86±4.35	8.81±0.12	49.48±7.08
	PLLA	163.53±16.89	20.22±1.02	607.34±66.41
70%	PLCL	1.60±0.29	0.27±0.046	170.62±14.13
	PLCL90PLLA10	62.40±6.13	7.47±0.56	23.32±2.21
	PLCL80PLLA20	67.89±13.41	6.99±1.20	19.81±0.66
	PLCL70PLLA30	72.44±16.34	9.98±2.27	37.64±13.49
	PLCL60PLLA40	76.97±6.33	9.80±1.37	40.07±4.95
	PLCL50PLLA50	163.53±16.89	20.22±1.02	607.34±66.41
	PLLA	228.04±20.41	25.27±1.94	1865.61±657.66

Note: Infill ratio, filling rate of 3D printing; E, elastic modulus; σ_{max}, compressive strength; $t_{1/2}$, stress relaxation time.

Based on Table 5, a table was re-made to display the effect of blend ratio of PLCL/PLLA on the mechanical properties of the 3D-printed scaffolds at same filling rate (Table S2).