Supplementary Materials

Superior Crystallization kinetics Caused by the Remarkable Nucleation Effect of Graphene Oxide in Novel Ternary Biodegradable Polymer Composites

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Friedman method to study the effective activation energy

The effective activation energies of the composites were also estimated. We used the isoconversion method proposed by Friedman[1,2] for relevant estimations. According to the Friedman method, the equation relating to the effective activation energy can be shown as the following equation,

$$ln\left(\frac{dX}{dt}\right)_{X,i} = Constant - \frac{\Delta E_X}{RT_{X,i}}$$

in the equation , at a specific conversion X, dX/dt represents the instantaneous crystallization rate as a function of time. ΔE_X is the effective activation energy at a specific conversion X and $T_{X,i}$ represents the temperatures correlated with a specific X at different cooling rates. The subscript i means each cooling rate used in the non-isothermal crystallization experiment. To estimate the effective activation energy, the X as a function of t can be obtained from the non-isothermal crystallization results. The value of dX/dt at a given X can be calculated by differentiating the obtained $X(t)$ function. The specific T_X value related to a given X can be further found according to the relationship among X, t, and T. By plotting the specific value of $ln(dX/dt)_{X,i}$ to $1/T_{X,i}$, the slope with a straight line plot can be used to estimate the effective activation energy ΔE_X. More detail descriptions on the estimation of the effective activation energy by the Friedman method can be found in the literatures.[2]

Table S1. Isothermal crystallization parameters evaluated by the Avrami equation for the PESu/PEG/GO=99/1/x composites. The x values are the relative weight ratios of GO in the composites and are 0, 0.5, 1, and 2.

PESu/PEG/GO (relative weight ratio)	T_c (^oC)	n	k (min^{-n})	$t_{0.5}$ (min)	$1/t_{0.5}$ (min^{-1})
100/0/0	50	2.52	0.0051	7.012	0.143
	52	2.55	0.0039	7.683	0.130
	54	2.38	0.0038	8.953	0.112
	56	2.49	0.0023	9.905	0.101
99/1/0	50	2.27	0.0166	5.183	0.193
	52	2.12	0.0161	5.917	0.169
	54	2.03	0.0144	6.736	0.148
	56	2.01	0.0111	7.797	0.128
99/1/0.5	50	2.61	0.0194	3.936	0.254
	52	2.44	0.0178	4.483	0.223
	54	2.22	0.0167	5.343	0.187
	56	2.21	0.0117	6.356	0.157
99/1/1	50	2.40	0.1516	1.884	0.531
	52	2.34	0.1065	2.226	0.449
	54	2.29	0.0709	2.709	0.369
	56	2.24	0.0458	3.365	0.297
99/1/2	50	2.18	0.2685	1.544	0.648
	52	2.20	0.1757	1.867	0.535
	54	2.18	0.1129	2.303	0.434
	56	2.13	0.0710	2.908	0.344

Table S2. Isothermal crystallization parameters evaluated by the Avrami equation for the PESu/PEG/GO=97/3/x composites. The x values are the relative weight ratios of GO in the composites and are 0, 0.5, 1, and 2.

PESu/PEG/GO (relative weight ratio)	T_c (°C)	n	k (min^{-n})	$t_{0.5}$ (min)	$1/t_{0.5}$ (min^{-1})
100/0/0	50	2.52	0.0051	7.012	0.143
	52	2.55	0.0039	7.683	0.130
	54	2.38	0.0038	8.953	0.112
	56	2.49	0.0023	9.905	0.101
97/3/0	50	2.59	0.0212	3.841	0.260
	52	2.49	0.0168	4.449	0.225
	54	2.36	0.0145	5.151	0.194
	56	2.21	0.0113	6.426	0.156
97/3/0.5	50	2.59	0.0366	3.115	0.321
	52	2.44	0.0272	3.766	0.266
	54	2.31	0.0221	4.459	0.224
	56	2.20	0.0161	5.551	0.180
97/3/1	50	2.51	0.2363	1.534	0.652
	52	2.50	0.1371	1.910	0.523
	54	2.39	0.0867	2.387	0.419
	56	2.30	0.0510	3.103	0.322
97/3/2	50	2.32	0.3151	1.405	0.712
	52	2.27	0.2189	1.661	0.602
	54	2.29	0.1317	2.063	0.485
	56	2.29	0.0828	2.532	0.395

Table S3. Isothermal crystallization parameters evaluated by the Avrami equation for the PESu/PEG/GO=95/5/x composites. The x values are the relative weight ratios of GO in the composites and are 0, 0.5, 1, and 2.

PESu/PEG/GO (relative weight ratio)	**T_c (^oC)**	**n**	**k (min^{-n})**	**$t_{0.5}$ (min)**	**$1/t_{0.5}$ (min^{-1})**
100/0/0	50	2.52	0.0051	7.012	0.143
	52	2.55	0.0039	7.683	0.130
	54	2.38	0.0038	8.953	0.112
	56	2.49	0.0023	9.905	0.101
95/5/0	50	2.22	0.0365	3.760	0.266
	52	2.25	0.0251	4.378	0.228
	54	2.19	0.0194	5.111	0.196
	56	2.14	0.0150	5.984	0.167
95/5/0.5	50	2.49	0.1266	1.982	0.505
	52	2.43	0.0865	2.359	0.424
	54	2.39	0.0586	2.808	0.356
	56	2.28	0.0406	3.476	0.288
95/5/1	50	2.17	0.3988	1.291	0.775
	52	2.17	0.2409	1.626	0.615
	54	2.10	0.1383	2.151	0.465
	56	2.04	0.0783	2.910	0.344
95/5/2	50	2.40	0.6841	1.005	0.995
	52	2.38	0.4407	1.209	0.827
	54	2.50	0.1964	1.656	0.604
	56	2.52	0.0980	2.176	0.460

Table S4. Non-isothermal crystallization parameters calculated by the Mo model for the PESu/PEG/GO=99/1/x composites. The x values are the relative weight ratios of GO in the composites and are 0, 0.5, 1, and 2.

PESu/PEG/GO (relative weight ratio)	X_t (%)	a	F(T)
100/0/0	20	1.09	20.18
	40	1.13	28.17
	60	1.16	35.88
	80	1.17	43.93
99/1/0	20	1.18	18.67
	40	1.18	26.32
	60	1.20	33.90
	80	1.22	42.73
99/1/0.5	20	1.01	13.52
	40	1.11	19.68
	60	1.21	27.35
	80	1.29	37.70
99/1/1	20	1.20	12.11
	40	1.31	18.05
	60	1.42	25.21
	80	1.53	36.86
99/1/2	20	1.03	10.03
	40	1.15	14.71
	60	1.27	20.64
	80	1.40	30.27

Table S5. Non-isothermal crystallization parameters calculated by the Mo model for the PESu/PEG/GO=97/3/x composites. The x values are the relative weight ratios of GO in the composites and are 0, 0.5, 1, and 2.

PESu/PEG/GO (relative weight ratio)	X_t (%)	a	F(T)
100/0/0	20	1.09	20.18
	40	1.13	28.17
	60	1.16	35.88
	80	1.17	43.93
97/3/0	20	1.05	18.33
	40	1.07	25.24
	60	1.08	31.51
	80	1.08	38.46
97/3/0.5	20	1.13	13.21
	40	1.20	19.44
	60	1.25	26.02
	80	1.28	34.52
97/3/1	20	1.09	10.91
	40	1.20	16.31
	60	1.29	22.72
	80	1.38	32.00
97/3/2	20	1.09	9.14
	40	1.16	13.56
	60	1.19	18.24
	80	1.19	23.70

Table S6. Non-isothermal crystallization parameters calculated by the Mo model for the PESu/PEG/GO=95/5/x composites. The x values are the relative weight ratios of GO in the composites and are 0, 0.5, 1, and 2.

PESu/PEG/GO (relative weight ratio)	**X_t (%)**	**a**	**F(T)**
100/0/0	20	1.09	20.18
	40	1.13	28.17
	60	1.16	35.88
	80	1.17	43.93
95/5/0	20	1.07	17.37
	40	1.11	24.54
	60	1.13	30.92
	80	1.14	38.37
95/5/0.5	20	1.09	12.83
	40	1.17	18.62
	60	1.24	25.06
	80	1.31	34.28
95/5/1	20	1.13	10.54
	40	1.22	15.4
	60	1.30	21.09
	80	1.39	29.42
95/5/2	20	1.24	7.851
	40	1.34	11.92
	60	1.41	16.28
	80	1.47	22.06

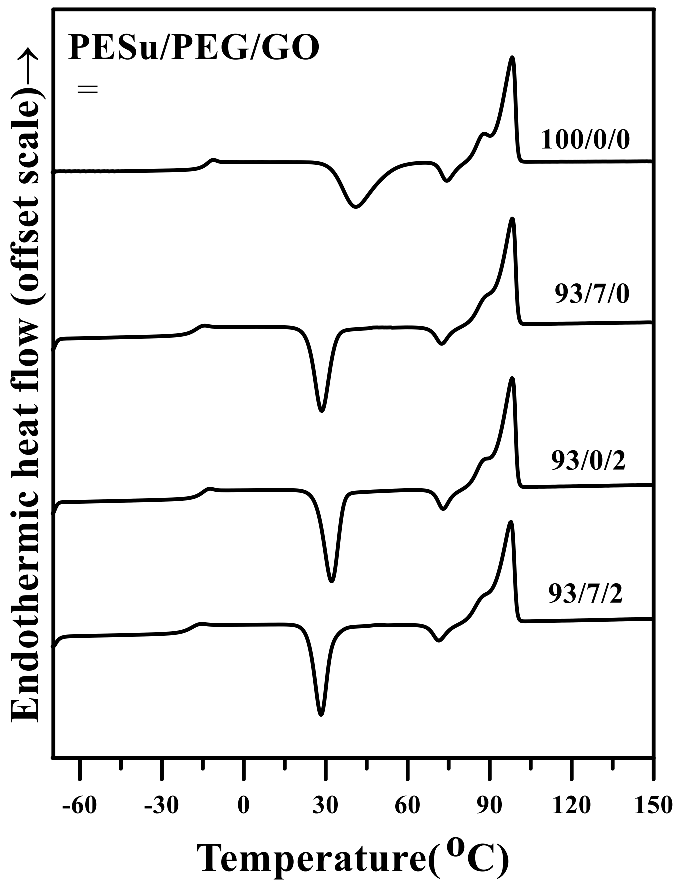

Figure S1. DSC thermal scans of neat PESu (coded as 100/0/0), binary PESu/PEG=93/7 blend (coded as 93/7/0), binary PESu/GO=93/2 composite (coded as 93/0/2) and ternary PESu/PEG/GO=93/7/2 composite (coded as 93/7/2).

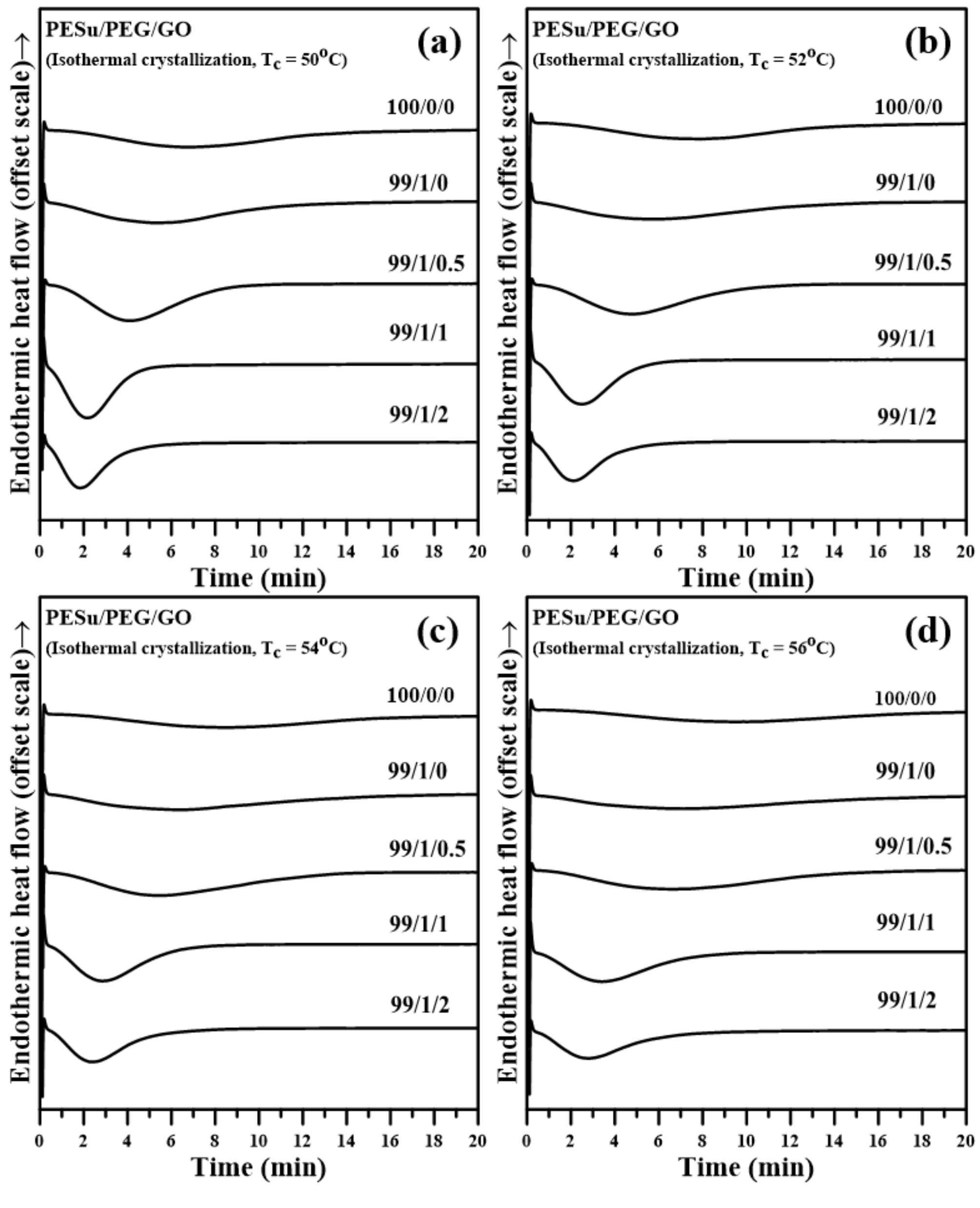

Figure S2. Isothermal crystallization thermograms of neat PESu and the PESu/PEG/GO=99/1/x composites at (a) T_c=50°C, (b) T_c=52°C, (c) T_c=54°C and (d) T_c=56°C. The x values are the relative weight ratios of GO in the composites and are 0, 0.5, 1, and 2.

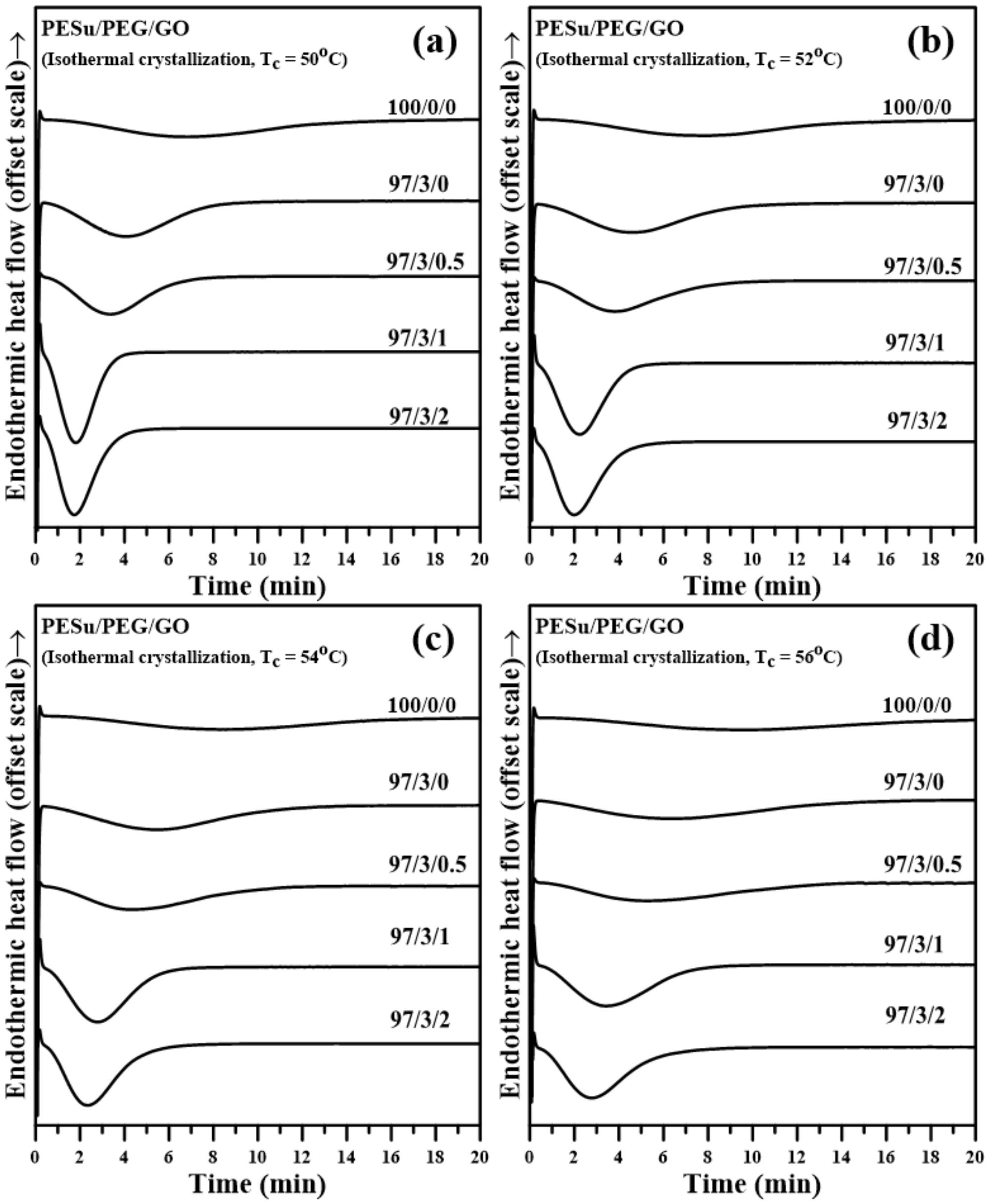

Figure S3. Isothermal crystallization thermograms of neat PESu and the PESu/PEG/GO=97/3/x composites at (a) T_c=50°C, (b) T_c=52°C, (c) T_c=54°C and (d) T_c=56°C. The x values are the relative weight ratios of GO in the composites and are 0, 0.5, 1, and 2.

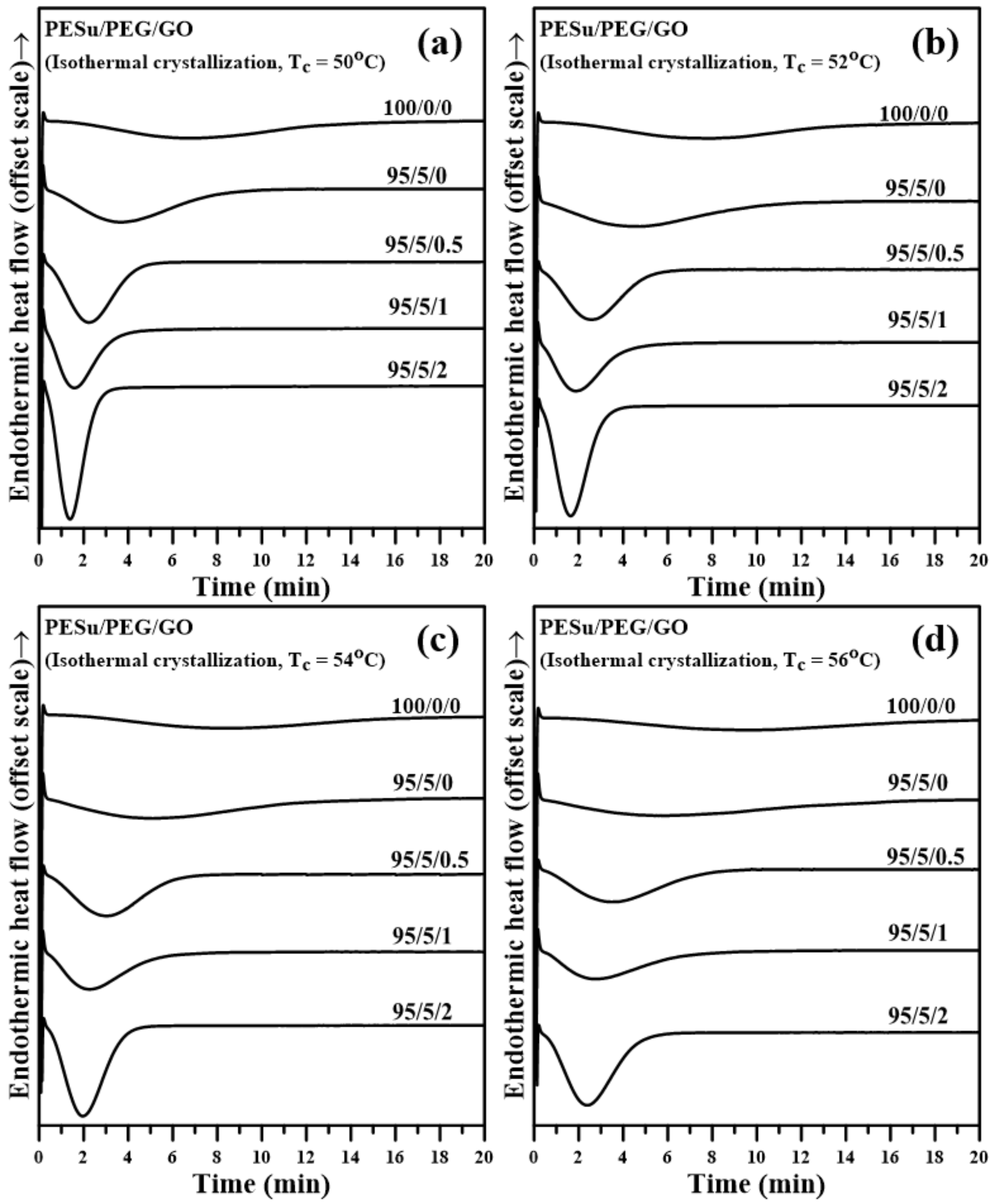

Figure S4. Isothermal crystallization thermograms of neat PESu and the PESu/PEG/GO=95/5/x composites at (a) T_c=50°C, (b) T_c=52°C, (c) T_c=54°C and (d) T_c=56°C. The x values are the relative weight ratios of GO in the composites and are 0, 0.5, 1, and 2.

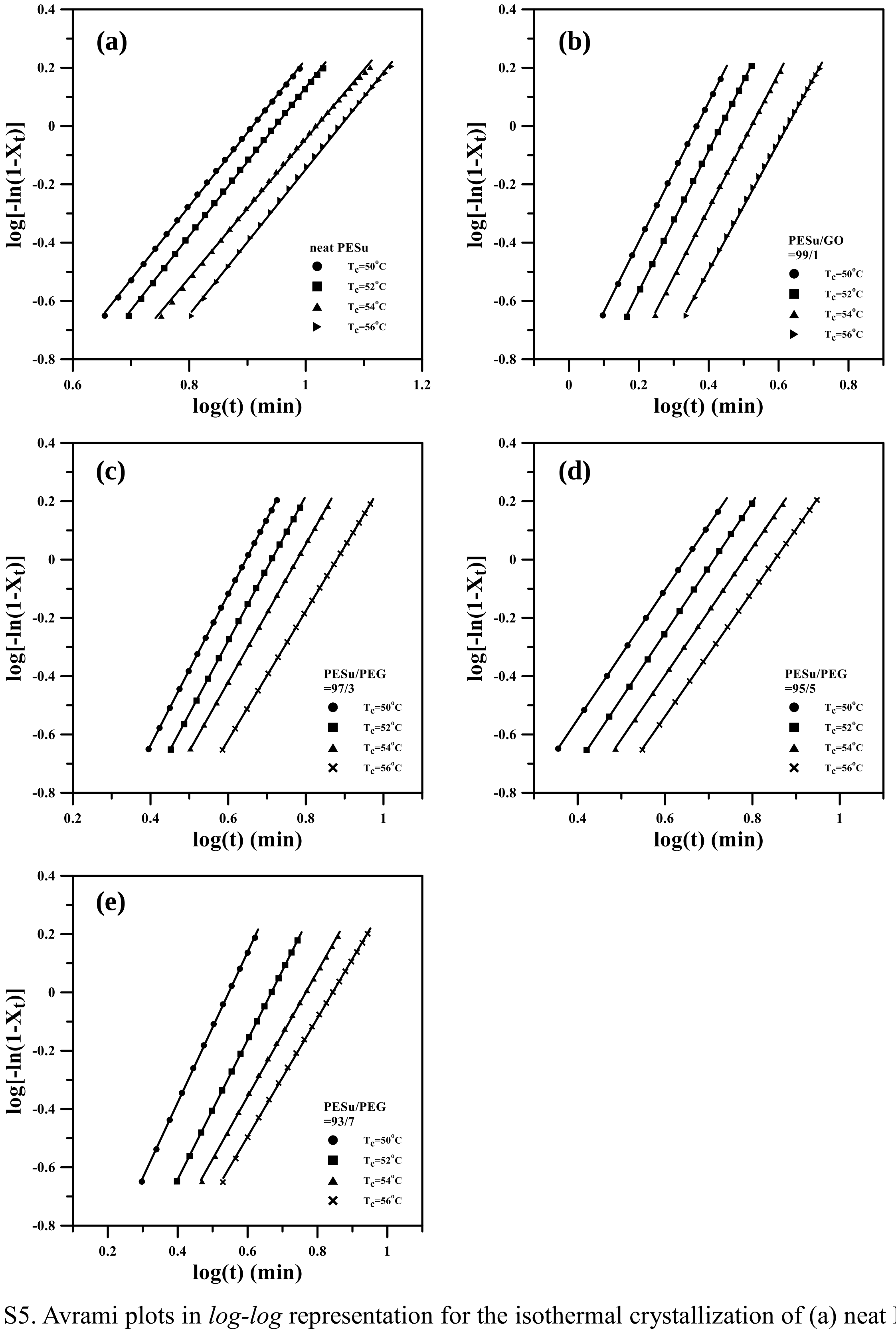

Figure S5. Avrami plots in *log-log* representation for the isothermal crystallization of (a) neat PESu, (b) PESu/PEG=99/1 blend, (c) PESu/PEG=97/3 blend, (d) PESu/PEG=95/5 blend, and (e) PESu/PEG=93/7 blend.

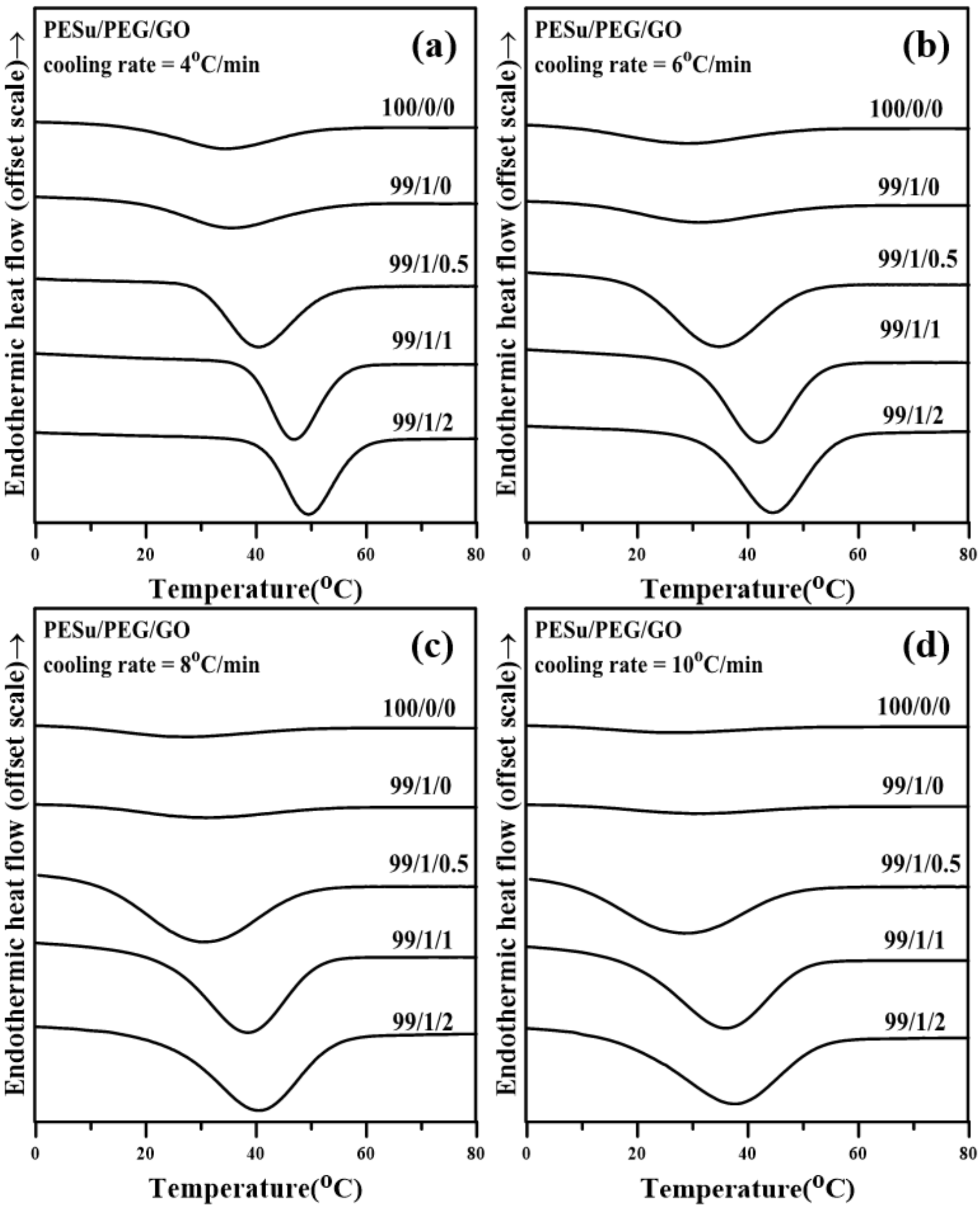

Figure S6. DSC non-isothermal crystallization results of neat PESu and the PESu/PEG/GO=99/1/x composites with a different cooling rate: (a) 4 ºC/min, (b) 6 ºC/min, (c) 8 ºC/min, and (d) 10 ºC/min. The x values are the relative weight ratios of GO in the composites and are 0, 0.5, 1, and 2.

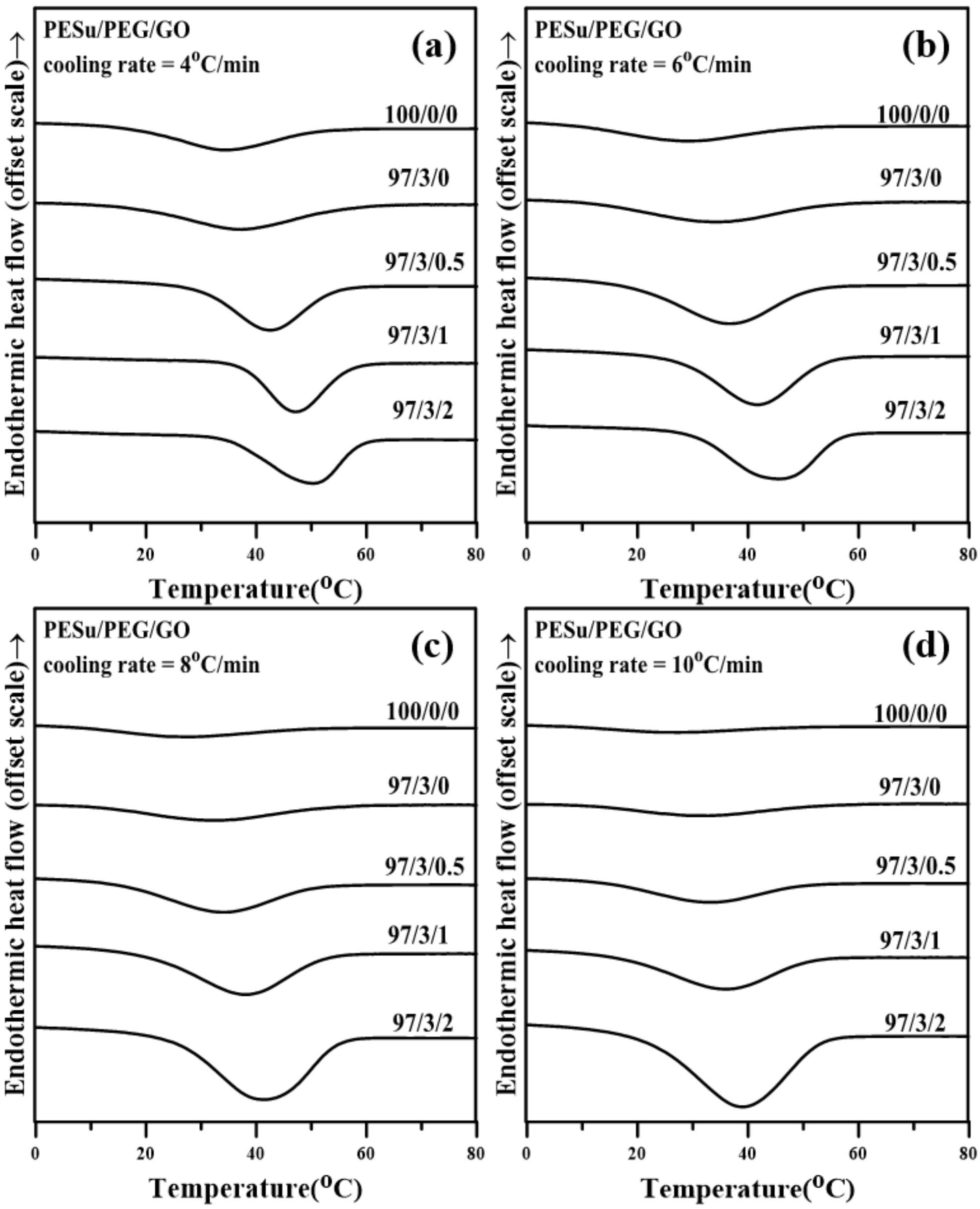

Figure S7. DSC non-isothermal crystallization results of neat PESu and the PESu/PEG/GO=97/3/x composites with a different cooling rate: (a) 4 ºC/min, (b) 6 ºC/min, (c) 8 ºC/min, and (d) 10 ºC/min. The x values are the relative weight ratios of GO in the composites and are 0, 0.5, 1, and 2.

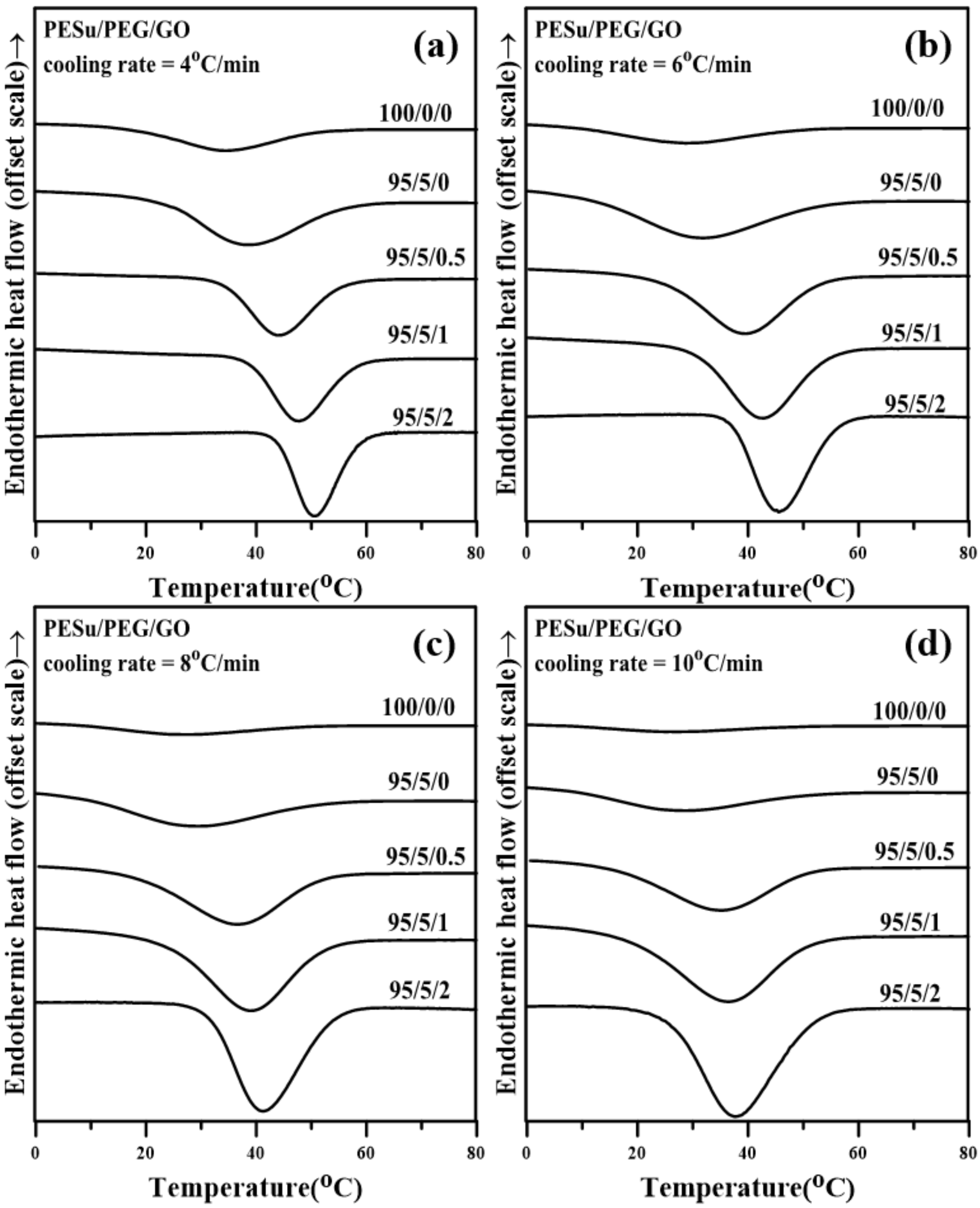

Figure S8. DSC non-isothermal crystallization results of neat PESu and the PESu/PEG/GO=95/5/x composites with a different cooling rate: (a) 4 ºC/min, (b) 6 ºC/min, (c) 8 ºC/min, and (d) 10 ºC/min. The x values are the relative weight ratios of GO in the composites and are 0, 0.5, 1, and 2.

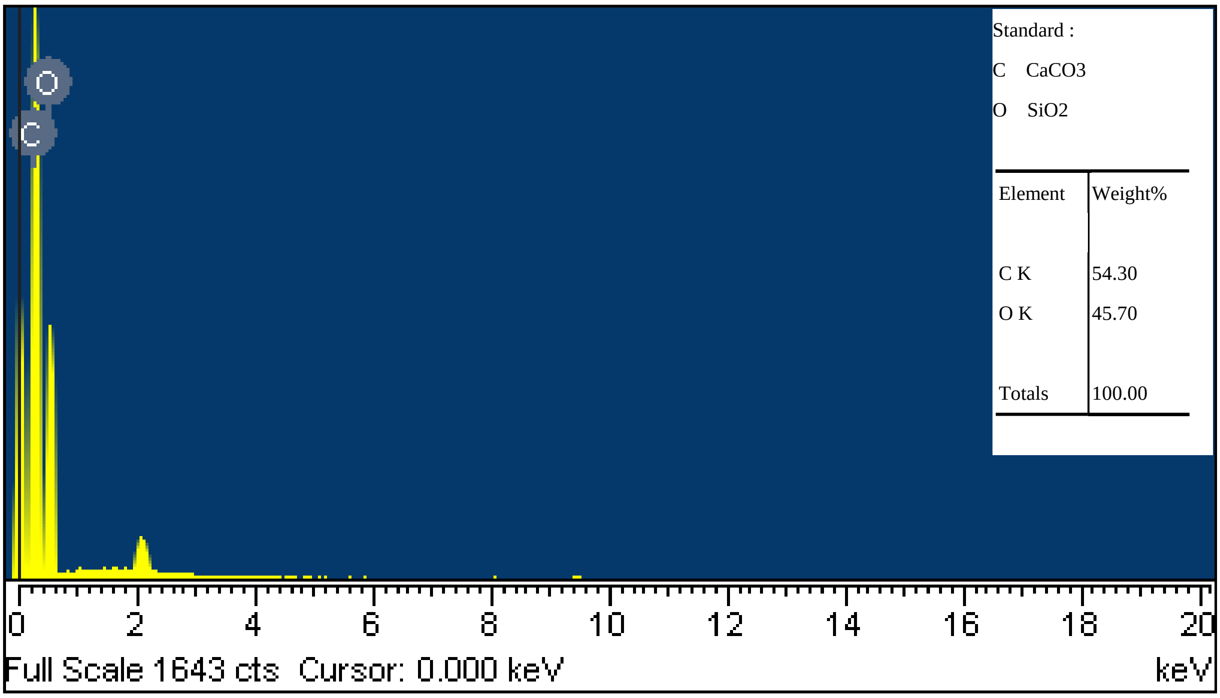

Figure S9. EDX results for PESu/PEG/GO=93/7/2 composite.

Reference of supplementary materials:

(1) Friedman, H. Kinetics of thermal degradation of char-forming plastics from thermogravimetry. Application to a phenolic plastic. *J. Polym. Sci. Part C* **1964**, *6*, 183–195.

(2) Vassiliou, A. A.; Papageorgiou, G. Z.; Achilias, D. S.; Bikiaris, D. N. Non-isothermal crystallisation kinetics of in situ prepared poly(ε-caprolactone)/surface-treated SiO_2 nanocomposites. *Macromol. Chem. Phys.* **2007**, *208*, 364–376.