

Article



Cold crystallization kinetics and thermal degradation of PLA composites with metal oxide nanofillers

Evangelia Tarani¹, Klementina Pušnik Črešnar², Lidija Fras Zemljič^{2*}, Konstantinos Chrissafis¹, George Z. Papageorgiou³, Dimitra Lambropoulou⁴, Alexandra Zamboulis⁵, Dimitrios N. Bikiaris⁵, Zoi Terzopoulou^{5*}

- 1 Department of Physics, Aristotle University of Thessaloniki, GR54124, Thessaloniki, Greece; etarani@physics.auth.gr (E.T.); hrisafis@physics.auth.gr (K.C.)
- 2 University of Maribor, Faculty of Mechanical Engineering, 2000 Maribor, Slovenia; klementina.pusnik@um.si (K.P.), lidija.fras@um.si (L.Z.)
- 3 Department of Chemistry, University of Ioannina, P.O. Box 1186, GR 45110 Ioannina, Greece; gzpap@uoi.gr (G.Z.P.)
- 4 Laboratory of Environmental Pollution Control, Department of Chemistry, Aristotle University of Thessaloniki, GR54124, Thessaloniki, Greece; dlambro@chem.auth.gr (D.L.)
- 5 Department of Chemistry, Laboratory of Chemistry and Technology of Polymers and Dyes, Aristotle University of Thessaloniki, GR54124 Thessaloniki, Greece, dbic@chem.auth.gr (D.N.B), azamboulis@gmail.com (A.Z.)
- * Correspondence: lidija.fras@um.si (L.Z.); terzozoi@chem.auth.gr (Z.T.)

Citation: Tarani, E.; Pušnik Črešnar, K.; Zemljič, L.F.; Chrissafis, K.; Papageorgiou, G.Z.; Lambropoulou, D.; Zamboulis, A.; Bikiaris, D.; Terzopoulou, Z. Cold Crystallization Kinetics and Thermal Degradation of PLA Composites with Metal Oxide Nanofillers. *Appl. Sci.* 2021, *11*, 3004.

https://doi.org/10.3390/app11073004

Academic Editor: Jordi Puiggalí

Received: 24 February 2021 Accepted: 23 March 2021 Published: 27 March 2021

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



Copyright: © 2021 by the authors. Submitted for possible open access publication under the terms and conditions of the Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/).

Supplementary data



Figure S1. DSC heating scans of PLA and its composites with heating rates (a) 2.5 °C/min, (b) 5 °C/min, (c) 7.5 °C/min, (d) 10 °C/min, (e) 15 °C/min, (f) 20 °C/min.



Figure S2. Relative crystallinity (*X*t) as a function of time during non-isothermal cold crystallization.



Figure S3. Ozawa plots of the non-isothermal cold crystallization of PLA and its nanocomposites.



Figure S4. Mo plots of the non-isothermal cold crystallization of PLA and its nanocomposites.



Figure S5. Kissinger plots for the non-isothermal cold crystallization of PLA and its nanocomposites.



Figure S6. Friedman plots of PLA and its nanocomposites.

Sample	Heating rate (°C/min)	T _g (°C)	$T_{cc}(^{\circ}C)$	DHcc (J/g)	$T_{m1}(^{\circ}C)$	$T_{m2}(^{\circ}C)$	DH _m (J/g)	Xc(%)
PLA	2.5	55	107.5	-26	147.2	154.9	26.9	28.9
	5	56.2	114.5	-25.6	148.4	154.1	21.4	23.0
	7.5	56.9	119.4	-15.6	149.2	-	15.3	16.5
	10	57.3	122.6	-9.8	149.7	-	10.4	11.2
	15	58.2	125.4	-3.86	150.3	-	4.5	4.8
	20	58.9	126.5	-1.7	150.5	-	2.2	2.4
PLA ZnO	2.5	54.6	100.8	-34.7	144.6	152.7	29.1	31.6
	5	54.5	113.3	-32.7	146.1	152.9	30	32.6
	7.5	55.1	122.1	-23.7	147.6	152.2	25.4	27.6
	10	55.6	127.6	-10.1	148.9	-	11.5	12.5
	15	56.1	129.6	-1.4	149.4	-	1.4	1.5
	20	56.6	132.5	-0.3	149.1	-	0.4	0.4
PLA Ag	2.5	54.9	101.7	-31.23	145.4	153.4	29.6	32.1
	5	55.8	109.2	-30.8	146.6	153.2	29.5	32.0
	7.5	57.1	115.2	-28.8	148	152.5	27.8	30.2
	10	57.4	120.6	-22.7	149.3	-	24	26.1
	15	58.2	127.1	-10.3	150.5	-	10.5	11.4
	20	59	129.4	-3	151	-	4.1	4.5
PLA TiO2	2.5	55.0	101.0	-29.3	145.1	153.3	26.3	28.6
	5	55.9	108.5	-28.9	146.0	153.0	26.0	28.2
	7.5	56.8	114.7	-27.2	147.3	152.7	25.5	27.7
	10	57.0	120.3	-21.4	148.3		22.9	24.9
	15	57.8	127.8	-8.4	150.1		8.7	9.4
	20	58.5	130.1	-2.2	150.5		2.3	2.5

Table S1. Thermal characteristics of PLA and its composites obtained from the DSC scans of Figure S1.

Table S2. Results of the Mo analysis of the non-isothermal cold crystallization of PLA and its nanocomposites.

Sample	PLA			PLA ZnO			PLA Ag			PLA TiO ₂		
Xt	lnF(t)	b	R ²	ln <i>F</i> (t)	b	R ²	lnF(t)	b	R ²	lnF(t)	b	R ²
0.2	2.96	1.22	0.86368	2.38	1.99	0.91251	2.27	1.21	0.91319	2.26	1.87	0.98734
0.4	3.31	1.24	0.89586	3.12	2.25	0.92377	2.67	1.30	0.93622	2.82	1.94	0.99504
0.6	3.55	1.24	0.91649	3.72	2.44	0.92741	2.96	1.35	0.94745	3.28	2.03	0.99618
0.8	3.74	1.21	0.93642	4.22	2.48	0.93512	3.25	1.40	0.95542	3.77	2.14	0.99512