Electronic Supplementary Information

Block-assembling: A New Strategy of Fabricating Conductive Nanoporous Materials from Nanocomposites Based on a Meltmiscible Crystalline/Crystalline Blend and MWCNTs

Lijun Ye, Cuicui Ye, Xianchun Shi, Hongyan Zhao, Kangyuan Xie, Depei Chen, Yongjin Li* College of Materials, Chemistry and Chemical Engineering, Hangzhou Normal University, Hangzhou 310036, People's Republic of China

*To whom correspondence should be addressed: yongjin-li@hznu.edu.cn



Fig. S1 Stress-elongation curves of PLLA/POM, PLLA/POM/CNTs nanocomposites with the indicated composites.

It can be seen from Fig. S1 that the modulus, yield strength and breaking strength of the PLLA/POM blends have been significantly enhanced with the addition of MWCNTs, implying the reinforcement effect of nanotubes on the blends. It is clear from Fig. S2 that two Tg's corresponded to PLLA and POM, respectively, are distinctly observed in the quenched samples of PLLA/POM and PLLA/POM/CNTs nanocomposites, indicating that PLLA and POM are phase-separated during the quenching process.



Fig. S2 Dynamic loss for the PLLA/POM blends as a function of temperature.



Fig. S3 LCST and UCST phase diagram for PLLA/POM blends as a function of composition.

Fig. S3 shows the phase diagram of PLLA/POM blends. PLLA/POM blends exhibit both LCST and UCST phase behaviors. In other words, PLLA and POM are miscible between the LCST and UCST temperatures. The crystallization temperatures of POM in the ternary nanocomposites are exhibited in Fig. S4 as well, which are slightly altered upon the varying of compositions. Moreover, it can be clear seen in Fig. S4 that all the temperatures of POM crystallization in the ternary nanocomposites are located between the LCST and UCST temperatures, implying that there has no phase separation occurring before and after POM crystallization. That is, all the POM components in the ternary nanocomposites crystallized in the miscible region and, furthermore, the crystallization of POM would not cause the phase separation of PLLA and POM.



Fig. S4 WARD patterns of neat PLLA, PLLA/POM (50/50) blends with different addition of MWCNTs, cooled in a 10 °C min⁻¹ rate from the melt state.

It is obvious that no diffraction peaks have been observed in the sample of neat PLLA, as shown in Fig. S4, indicating that PLLA chains are still in an amorphous state when being cooled from the melt state in a 10 °C min⁻¹ cooling rate. Moreover, no diffraction peak can be found in the samples of PLLA/POM (50/50) blends with different addition of MWCNTs, either. It can be concluded that the PLLA components in PLLA/POM (50/50) blends with addition of MWCNTs (from 0.1 wt % to 1.0 wt %) cannot crystallize in a cooling rate of 10 °C min⁻¹ from the melt state.



Fig. S5 WARD pattern of PLLA/POM/MWCNTs (70/30/1.0) nanocomposite cooled in a 10 °C min⁻¹ rate from the melt state.

Fig. S5 shows the WAXD pattern of PLLA/POM/MWCNTs (70/30/1.0) nanocomposite cooled in a 10 °C min⁻¹ from the melt state. The crystal diffraction peaks at $2\theta = 14.8$ °, 16.7 °, 18.9 ° and 22.1 ° are, respectively, assigned to the (010), (110/200), (203) and (015) lattice planes of PLLA α -form crystals, implying the crystallization of PLLA in the PLLA/POM/MWCNTs (70/30/1.0) nanocomposite. Therefore, the two exothermic peaks observed from the DSC cooling curves in Fig. 4 are corresponding to the crystallization of PLLA (the lower one) and POM, respectively.

Table.	S 1	Nonisothermal	crystallization	properties	of	PLLA/POM/MWCNTs	nanocomposites	with	the	indicated
compo	sitio	ıs.								

Sample Name	Т _{с, РОМ} (°С)	ΔH _{с, POM} (J/g)	X _{c, POM} (%)
PLLA/POM/CNTs=50/50/0.1	150.0	66.29	69.85
PLLA/POM/CNTs=50/50/0.5	151.1	66.89	70.77
PLLA/POM/CNTs=50/50/1.0	151.8	66.15	70.33

Blending Ratio (PLLAPOM/MWCNTs)	T _{c, POM} (°C)	T _{c, PLLA} (°C)	ΔН _{с, РОМ} (J/g)	ΔH _{c, PLLA} (J/g)	Х _{с, РОМ} (%)	X _{c, PLLA} (%)
0/100/1.0	150.6		128.70		68.41	
10/90/1.0	150.5		120.1		70.94	-
30/70/1.0	151.8		91.29		69.33	
50/50/1.0	151.8		66.15		70.33	
60/40/1.0	152.0	106.7	53.09	6.478	70.55	11.73
70/30/1.0	152.0	114.0	37.13	16.99	69.79	26.36
80/20/1.0	151.6	117.0	24.33	21.89	69.67	29.72
90/10/1.0	151.5	120.7	13.30	26.46	70.70	31.93
93/7/1.0	151.5	119.4	9.521	26.54	71.30	30.99
95/5/1.0	151.3	121.8	6.596	27.23	70.13	31.13
97/3/1.0	151.2	122.7	4.070	29.35	71.12	32.86
99/1/1.0	149.6	122.4	1.186	29.70	63.05	32.58
100/0/1.0		123.7		32.09		34.85

Table. S2 Nonisothermal crystallization properties of PLLA/POM/MWCNTs nanocomposites with 1.0 wt % loading of MWCNTs.

It is clear seen from Table. S1, the crystallization rate (v_c) and crystallinity (X_c) of POM in PLLA/POM blends slightly changed, with the addition of MWCNTs. It comes to conclude that the coverage rate of MWCNTs will probably decrease with the increasing amount of MWCNTs, leading to the enlargement of spacing between the adjacent kebab crystals. Moreover, the v_c and X_c keep almost constant, as shown in Table. S2. It might be attributed to the "saturation" of MWCNTs for nucleating the POM crystallization. In other words, the loading of MWCNTs is adequate for the POM crystallization in the ternary nanocomposites, and further, no completely but partially covered nanotubes are left after the crystallizing of POM. It is further to found that the v_c and X_c of PLLA are significantly enhanced, with the increasing concentration of PLLA. It might be ascribed to the increasing amount of nucleating sites left in the intra-NHSK regimes and the extending of the spacing between the adjacent kebab POM crystals, due to the decreasing of POM concentration.



Fig. S6 Time-resolved FTIR spectra of the PLLA/POM/MWCNTs (90/10/1.0) nanocomposite during isothermal crystallization of PLLA at 140 °C (0-300 s).

It can be seen from Fig. S6 that the 1210 cm⁻¹ band exhibits a faster and more sensitive response to inter-chain conformational ordering than the 1456 cm⁻¹ one. The band at 1210 cm⁻¹ is generally corresponded to the combination of –COC- and -CH3 inter-chain interaction of PLLA and assigned to an E1 mode (perpendicular to the helix axis) and its intensity increases because the transition moments corresponding to the conformers change their orientation from a random arrangement to an *in-plane* orientation (formation of crystal planes).¹ According to work reported by Li et al, the intensity increase is originated from the unique template effect of CNTs on the conformational ordering of PLLA.^{2, 3}



Fig. S7 Azimuthal profiles of PLLA $\alpha(110/200)$ and POM (100) reflections and the 2-D WAXD pattern of the PLLA/POM/MWCNTs (70/30/1.0) nanocomposite cooled in a 10 °C min⁻¹ rate from the melt state.

The PLLA/POM/MWCNTs (70/30/1.0) sample for 2-D WAXD measurement is pre-oriented by a simple melt-stretching process. The reflections in the 2D WAXD pattern (the right image in Fig. S7) from

the inner to outward are assigned to (110/200), (203) crystal planes of PLLA α -form and (100) plane of POM crystals, corresponding to the 2 θ value of 16.7 °, 18.9 °, 22.7 °, respectively. Note that, the direction of the flow field (the axes of MWCNTs) is marked and placed to be horizontal during the 2-D WARD measurements. Although the orientation degree of the 70/30/1.0 sample (oriented just by the manual melt-stretching) is low, the weak but distinguishable diffraction arcs of POM (100) crystal planes appear in the vertical direction (the azimuth angle are 90 ° and 270 °, respectively), indicating that POM molecular chains are parallel to the axes of MWCNTs. Moreover, the similar diffraction arcs of the PLLA α (110/200) crystal planes are observed as well in the vertical direction, implying that the PLLA molecular chains are oriented to be parallel to the POM ones as well as the axes of nanotubes (that is, the PLLA and POM lamellae are in the same orientation). These results again indicate that both of the POM and PLLA molecular chains are nucleated by MWCNTs, resulting in a "block-assembling" of nanotubes to form the THSK superstructures in PLLA/POM/MWCNTs ternary nanocomposites.



Fig. S8 Macroscopic image for the extraction solution of the PLLA/POM/MWCNTs ternary nanocomposites.

It is clear from Fig. S8, the extracted solution always keeps colorless and transparent, implying that majority of MWCNTs are still contained in the residue materials.

References

- 1. E. Meaurio, N. Lo'pez-Rodriguez, J. R. Sarasua, Macromolecules, 2006, 39, 9291.
- J. Z. Xu, T. Chen, C. L. Yang, Z. M. Li, Y. M. Mao, B. Q. Zeng, B. S. Hsiao, *Macromolecules*, 2010, 43, 5000.
- 3. X. Hu, H. N. An, Z. M. Li, Y. Geng, L. B. Li, C. L. Yang, Macromolecules, 2009, 42, 3215.