Electronic Supplementary Information (ESI) for

"Ultralow Percolation Threshold and Enhanced Electromagnetic Interference Shielding in Poly($_{\text{L}}$-lactide)/Multi-Walled Carbon Nanotubes Nanocomposites with Electrically Conductive Segregated networks"

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1. Transcrystals in S-PLLA/MWCNTs composites

The cryo-fractured surface of the S-PLLA/MWCNTs composites was etched in a water-methanol (1/2 v/v) solution containing 0.025 mol/L sodium hydroxide to remove the amorphous regions of the PLLA matrix, and finally coated with a layer of platinum in a vacuum chamber before the SEM observation. Fig. S1 shows the crystalline morphology of the S-PLLA/MWCNTs composites with 0.6 vol. % MWCNTs. It can be found that the transcrystalline layers and spherulites range in the H-PLLA phase. The transcrystals which was formed by the nucleating effect of MWCNTs were surrounded with the L-PLANT phase. The formation of the transcrystals was thought to enhance the Young's modulus and tensile strength of S-PLLA/MWCNTs composites.

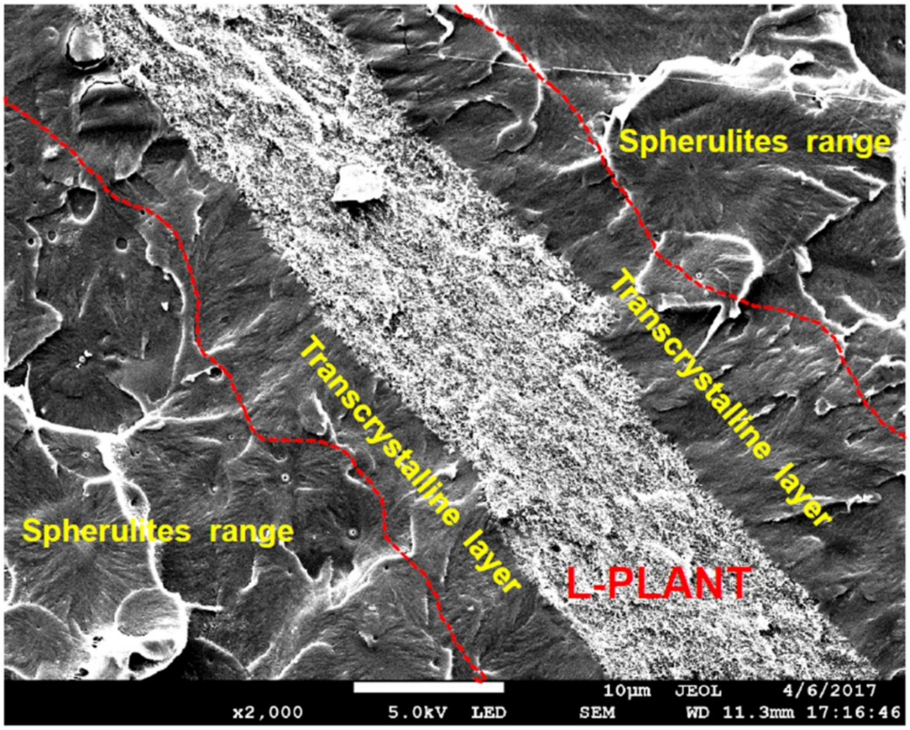

Fig. S1 Crystalline morphology of the S-PLLA/MWCNTs composites with 0.6 vol. % MWCNTs.

2. Nonisothermal crystallization behavior of the S-PLLA/MWCNTs composites

The nonisothermal crystallization behavior of the samples was performed by a differential scanning calorimeter (NETZSCH DSC-214) in a dry nitrogen atmosphere. For each measurement, about 5 mg sample was placed in an aluminum pan, which was first heated from 25 to 190 °C at a heating rate of 10 °C/min and held for 5 min to remove thermal history, then cooled down to 25 °C at a cooling rate of 10 °C/min, and finally reheated to190 °C at a heating rate of 10 °C/min. The degree of crystallinity (X_c) was evaluated according to the Eq. S1 from the second heating curve.[S1]

$$X_c = \frac{\Delta \mathrm{H}_m - \Delta \mathrm{H}_c}{w_f \Delta \mathrm{H}_m^o} \tag{S1}$$

where $\Delta \mathrm{H}_m$, $\Delta \mathrm{H}_c$, w_f and $\Delta \mathrm{H}_m^o$ were the measured enthalpies of melting, the measured enthalpies of cold crystallization, the weight percent of PLLA matrix and the melting enthalpies of 100 % crystalline PLLA of 93.7 J/g,[S2] respectively.

Fig. S2 shows the non-isothermal crystallization of the L-PLANT, R-PLLA/MWCNTs and S-PLLA/MWCNTs composites. The L-PLANT composites have only one thermal transition upon heating, i.e. glass transition at ~ 60 ^{o}C, indicating that no crystallization for L-PLLA happens during the processing. However, both the R-PLLA/MWCNTs and S-PLLA/MWCNTs composites exhibit multiple transitions upon heating: a glass transition temperature (T_g) of ~ 60 ^{o}C, a cold crystallization peak (P_{cc}) of ~115 ^{o}C and a melting peak (P_m) of ~170 ^{o}C. The crystallinity of the composites was also calculated and showed in Fig. S2b and c. The crystallinity of all the tested S-PLLA/MWCNTs composites was less than 7 %, while the tested R-PLLA/MWCNTs composites had more than 13 % crystallinity. The reasons are that the MWCNTs show high nucleating effect on H-PLLA crystallization but no nucleating effect on L-PLLA crystallization (Fig S2a). The nucleating effect on H-PLLA crystallization is also retarded by the confined distribution of MWCNTs in L-PLLA phase for the S-PLLA/MWCNTs composites. Furthermore, the crystallinity of the R-PLLA/MWCNTs composites increases at low MWCNTs loadings (0, 0.2 and 0.6 vol. %) and then decrease at high MWCNTs loadings (0.8 vol.%). The results are attributed to the crystallization confinement probably happening at the higher concentration of MWCNTs.

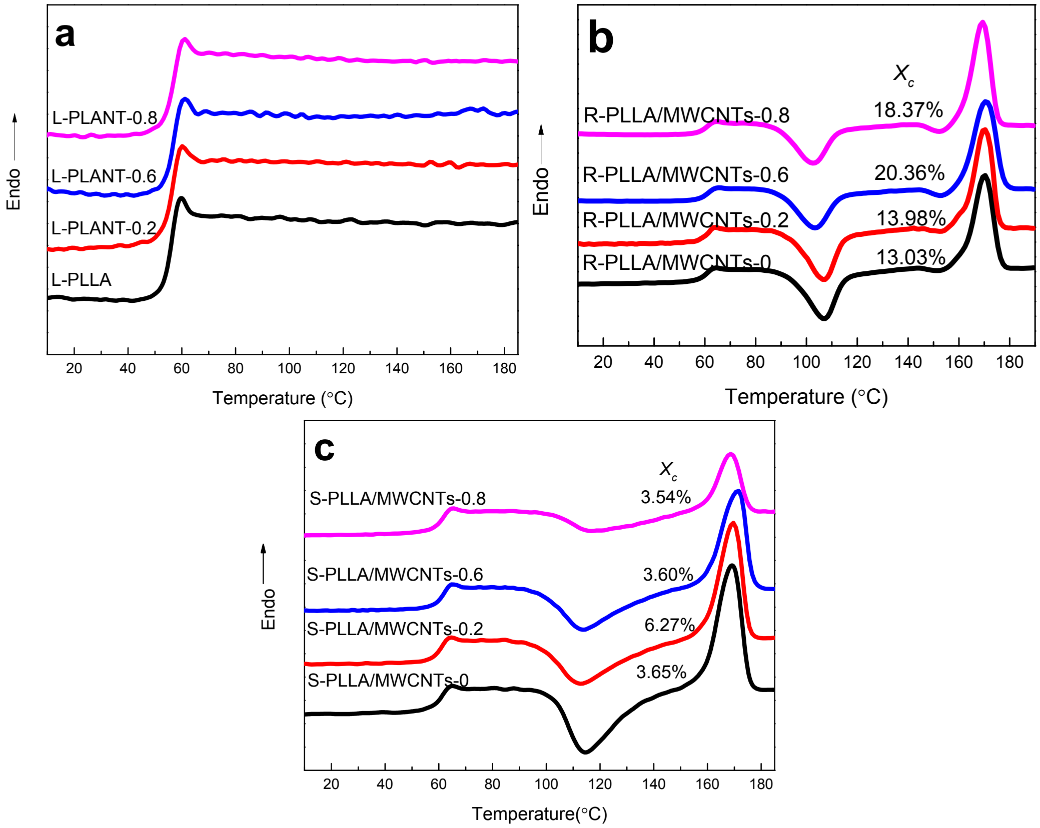

Fig. S2 DSC and heating curves of the L-PLANT (a), R-PLLA/MWCNTs (b) and S-PLLA/MWCNTs (c) composites s with different MWCNTs loadings.

References

S1. Y.-D. Shi, M. Lei, Y.-F. Chen, K. Zhang, J.-B. Zeng, M. Wang, *J. Phys. Chem. C*, 2017, **121**, 3087-3098.

S2. D.A. Garlotta, *J. Polym. Environ.*, 2001, **9**, 63-84.