

Electronic Supplementary Information(ESI)

Morphological diagram of nucleating agent/poly(ϵ -caprolatone) and in-situ barriering strategy

Siqi Wu, Rui Han, Min Nie*, Qi Wang

Address: State Key Laboratory of Polymer Materials Engineering, Polymer Research Institute of Sichuan University, Chengdu 610065, China

Email: poly.nie@gmail.com

Fax: +86-28-85402465

Tel: +86-28-85405133

Materials

Poly(ϵ -caprolatone)(trade name: Esun600C) was supplied by Shenzhen Esun Industrial Co., Ltd.(Shenzhen, China). Its melt flow index was 10g/10min (2.16kg, 150°C).

TMB-5(NAs), aryl amide-based compound, was provided by Shanxi Provincial Institute of Chemical Industry(Shanxi, China). It had similar chemical structure to N,N'-dicyclohexyl-2,6-naphthalene dicarboxamide.

Sample preparation

PCL/NAs blends contained different concentrations of NAs were compounded in a corotating twin screw extruder. The extruded temperature was 100°C and the screw

speed was 30 r/min.

Characterization

Thermal gravimetric analysis (TGA) of PCL was performed by using TA Instruments(TGA Q50) under nitrogen atmosphere. The sample was heated from 25 to 600°C with a heating rate of 10 °C/min.

Differential scanning calorimetry (DSC) analysis was conducted by a Q20 differential scanning calorimetry apparatus (TA, America). The ~7 mg specimens were heated from 0 to 240°C at the 10°C/min heating rate under nitrogen atmosphere. In order to investigating the effects of NAs on the crystallization behaviors of PCL, the specimens were cooled down at a cooling rate of 10 °C/min.

The crystalline structure of PCL and NAs were investigated by using wide-angle X-ray diffractometer (DX-1000, Dandong Fangyuan Instrument Co., Ltd, China). CuK α radiation was conducted at 40 kV and 25 mA. The scanning 2 θ range was 10~30° and the scanning rate was 2°/s.

The phase-transformation behaviors of the PCL/NAs blends with the different NAs concentrations were observed and the morphology of NAs was recorded using a Leica DM2500P polarized light microscope (PLM) equipped with a hot stage(THMS600). The samples were heated at a constant heating rate of 10°C/min to the desired temperature and cooled at a cooling rate of 10°C/min to 20°C.

Dissolution and solidification of NAs

The complete dissolution and solidification temperatures of NAs were presented in Figure 1S. With the increasing content of NAs, the dissolution and solidification temperature did rise significantly. It can be ascribed to the limited liquid miscibility and high solid immiscibility between PCL and NAs¹. The similar results were also reported by other researchers^{2, 3}. Compared to the two temperature in Figure 2, the dissolution temperature was higher than the formed temperatures of fiber-like NAs and exhibited almost same as that where flake-like NAs were generated, suggesting that the solubility of NAs dictated the morphology formed during the subsequent cooling process.

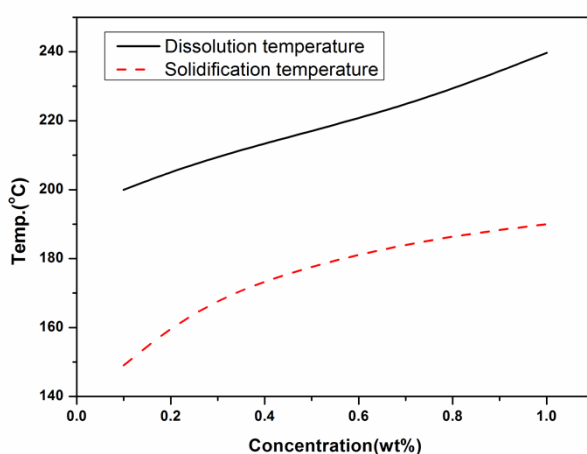


Figure 1S The dissolution and solidification temperatures of PCL/NAs blends.

TGA analysis

Figure 2S presented TGA weight loss curve of PCL. Clearly, the thermal decomposition temperature of PCL was higher than 300°C, which was consistent with the temperature reported by other research⁴, so PCL could not degrade at the formed temperature of flake NAs (~230°C).

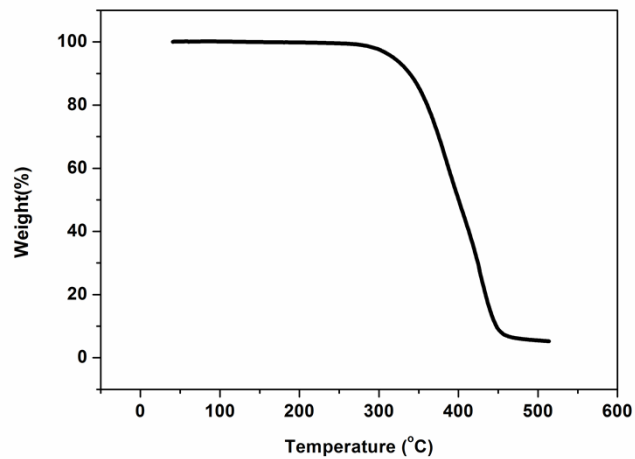


Figure 2S TGA weight loss curve of PCL

DSC analysis

Figure 3S was DSC heating curves of PCL with different NAs concentrations. Clearly, all samples only displayed a single sharp melting peak of PCL at $\sim 65.5^{\circ}\text{C}$ and the enthalpy nearly unchanged when temperature was increased to 240°C , indicating PCL kept stable and the reaction didn't occur between NA and PCL at the temperature range.

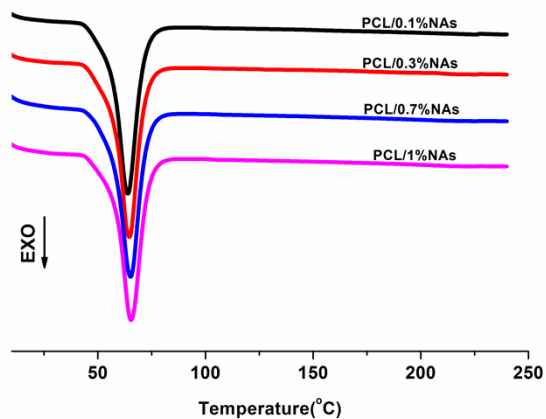


Figure 3S DSC heating curves of PCL with different NAs concentrations

XRD analysis

When polymer and additive have similar d-spacing, the later has good ability to nucleate the former, i.e., the polymer tends to grow on the surface of the additive⁴. The epitaxial disregistry (D) between the two materials can be calculated based on the following equation⁵:

$$D=(d_{\text{polymer}}-d_{\text{additive}})/ d_{\text{additive}} \times 100\%$$

where d_{polymer} and d_{additive} are the d-spacings of polymer and additive, respectively. For epitaxial crystallization, the usually accepted disregistry is lower than 10%. In order to demonstrate the nucleating mechanisms of TMB-5 on PCL, XRD experiments of PCL and NAs were conducted, as shown in Figure 4S. The results indicated that $d_{(110)}$ of PCL was 0.41nm while TMB-5 had the strong reflection located at the d-spacing of 0.41nm. The perfect matching was found between the two materials, suggesting the epitaxial interaction between PCL and TMB-5. Therefore, it seemed reasonable that TMB-5 could promote the crystallization of PCL greatly, which was also proved by the increased crystallization temperature of PCL with the presence of TMB-5.

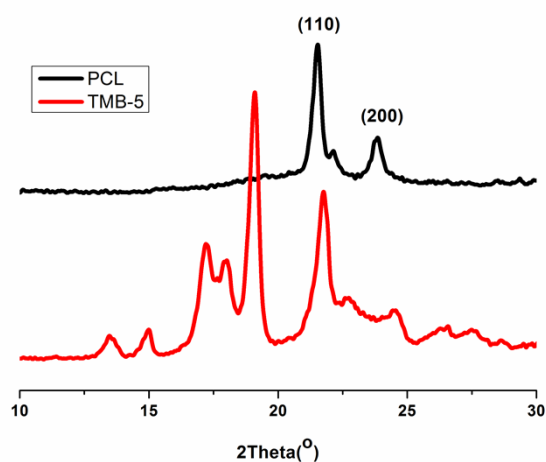


Figure 4S XRD curves of PCL and TMB-5

References

1. Z. Horvath, B. Gyarmati, A. Menyhard, P. Doshev, M. Gahleitner, J. Varga and B. Pukanszky, *RSC Adv*, 2014, **4**, 19737.
2. Y. Fan, J. Zhu, S. Yan, X. Chen and J. Yin, *Polymer*, 2015, **67**, 63.
3. M. Yamaguchi, T. Fukui, K. Okamoto, S. Sasaki, Y. Uchiyama and C. Ueoka, *Polymer*, 2009, **50**, 1497.
4. H. Peng, Y. Han, T. Liu, W. C. Tjiu and C. He, *Thermochim Acta*, 2010, **502**, 1.
5. M. L. Minus, H. G. Chae and S. Kumar, *Macromol Rap Commun*, 2010, **31**, 310.
6. J. C. Wittmann and B. Lotz, *J Polym Sci: Polym Phys Edit*, 1981, **19**, 1837.