

## Supporting Information

### **Soft-Hard Dual Nanophases: A Facile Strategy for Polymer Strengthening and Toughening**

Guangyao Ji, Mingyu Sang, Xuhui Zhang,\* Jing Huang, Ting Li, Yang Wang, Shibo Wang, Weifu Dong\*

The Key Laboratory of Synthetic and Biological Colloids, Ministry of Education, School of Chemical and Material Engineering, Jiangnan University, 1800 Lihu Road, Wuxi 214122, China

\*E-mail: xuhuizhang@jiangnan.edu.cn; wfdong@jiangnan.edu.cn

Tel.: +86-510-8532-6290. Fax: +86-510-8591-7763.

### **Experimental Section**

**Materials.** PLA (4032D, 98% L-lactide content) was purchased from NatureWorks (USA). Tannic acid (TA, analytically pure), propylene carbonate (PC, with a purity of 99%) and sodium hydroxide (NaOH, analytically pure) were purchased from Aladdin (Shanghai). Alcohol and chloroform (CHCl<sub>3</sub>, analytically pure) were purchased from Sinopharm Chemical Reagent Co., LTD.

**Preparation of mTA.** In a 250 ml three-necked flask, 10 g TA (0.15 mol OH), 0.6 g NaOH (0.015mol) and 230 g PC (2.25mol) were added. With continuous nitrogen purging and mechanical agitation, the mixture was heated to 170°C for the hydroxyalkylation reaction and the reaction lasted for 10 h. After cooling, the resulting sticky liquid was diluted by 50 ml ethanol, followed by being transferred to a dialysis bag with an interception molecular weight greater than 1000 Da. The dialysis proceeded in deionized water and the water is changed every day. After replacing the water for 5 times, the dark brown liquid at the bottom of the dialysis bag was separated and dried to a constant weight under 60°C.

---

The resulting mTA is a kind of sticky dark brown liquid.

**Preparation of dual-nanophase PLA.** 10 g PLA, 1.0 g mTA and 100 ml CHCl<sub>3</sub> were added to a conical flask (250 mL) and the mixture was stirred at room temperature for 4 hours to obtain a uniform PLA/mTA solution. The solvent was removed by rotary evaporation at 35 °C and vacuum drying at 45 °C successively to obtain dried PLA/mTA composite. Then the PLA/h-mTA10 composite was hot-pressed at 180°C to obtain the plasticized PLA which was in the form of sheet with a thickness of 0.5 mm. Subsequently, the plasticized PLA was transferred to a vacuum oven at 100 °C for 4 min to obtain the dual-nanophase PLA.

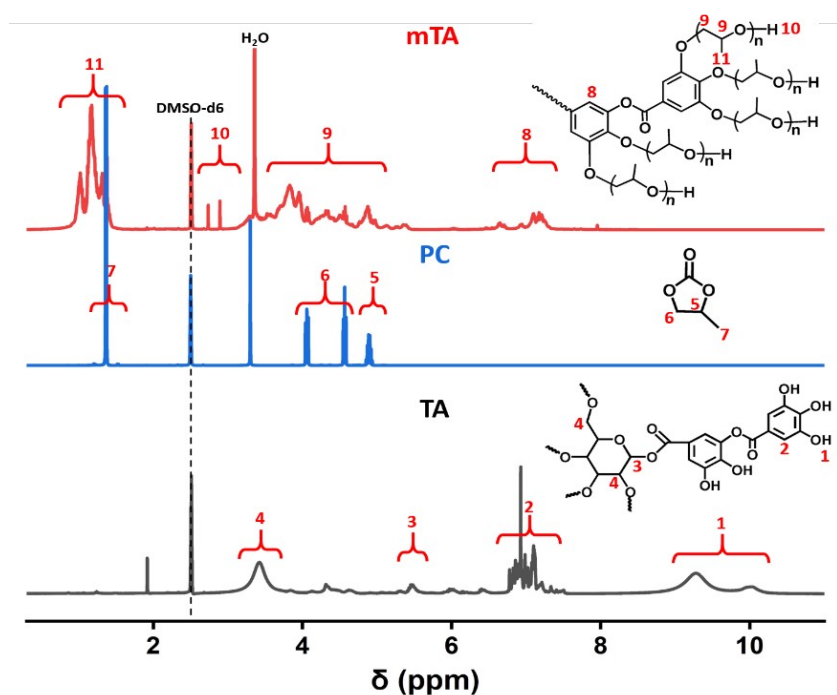
**Characterization.** Quantitative <sup>1</sup>H NMR spectra of TA and mTA were recorded on a Bruker 400 MHz spectrometer (32 scans at 25 °C) with a solvent of DMSO-d<sub>6</sub>. FTIR spectra of TA, mTA, PLA and PLA/mTA were recorded on an FTIR spectrometer (Nicolet 6700, United States) with a scan times of 16 and a resolution of 4 cm<sup>-1</sup>. The microstructure of the plasticized PLA and the dual-nanophase PLA were observed by atomic force microscope (AFM, MuLtimode 8, Bruker Technology GMBH, Germany). The specimens for AFM measurement were prepared by freezing slice. Differential scanning calorimetry (DSC) curves were measured by using a DSC analyzer (Perkin Elmer DSC-8000, USA). The heating/cooling rate for all samples were set as 10°C/min. For PLA-containing samples, the temperature range was 10~180 °C and the first heating curves without removing heat history were adopted for the crystallinity calculation and T<sub>cc-i</sub> determination. For neat mTA, the temperature range is -20~80 °C and the second heating curve with removed heat history was adopted to determine the T<sub>g</sub> of mTA. Polarized optical micrographs of PLA-containing samples were recorded by polarized optical microscopy (POM, Axio Imager A2POL, Germany/UK). The X-ray diffraction profiles were measured by X-ray diffractometer (D8, Bruck AXS Technology GMBH, Germany). Gel permeation

---

chromatography (GPC, 1515, USA) was performed to measure the molecular weight of PLA. The eluent is tetrahydrofuran with a flow rate of 1 mL/min and a polystyrene (PS) standard is used for calibration. Images of the cryo-fractured surfaces, surface, tensile fracture-surface of PLA-containing samples were recorded by scanning electron microscope (SEM, Hitachi S-4800, Japan). The tensile properties of all samples were measured using a tensile testing machine (US Instron 5967) and dumbbell type specimens following ASTM D 412. The test temperature was 25°C and the tensile rate was 5 mm/min. At least five specimens for each sample were recorded to make sure data accuracy and repeatability. Then the toughness, the work required per unit volume of sample to break, is calculated by the equation (1):

$$W = \int_{\varepsilon=0}^{\varepsilon=\varepsilon_{\max}} \sigma d\varepsilon \quad (1)$$

where  $\sigma$  is the stress (MPa) and  $\varepsilon$  is the displacement (mm/mm).

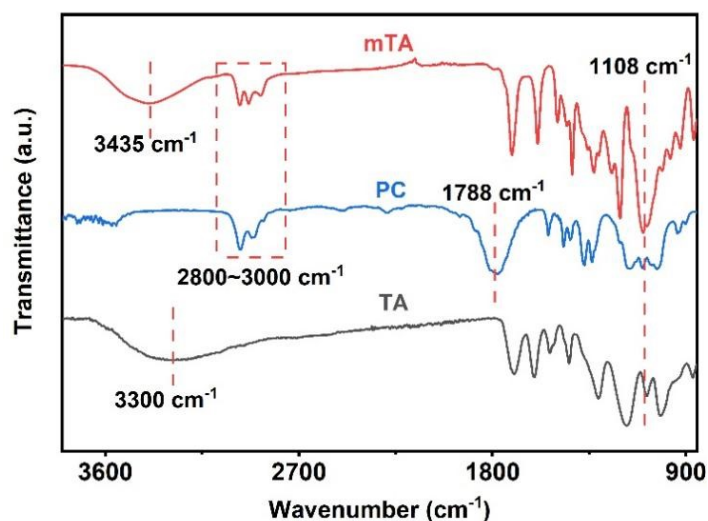


**Figure S1.**  $^1\text{H}$  NMR of TA, PC and mTA. The solvent is DMSO- $d_6$ . For TA, peak 1 locating at 9.2~10.2 ppm relates to proton in the phenol hydroxyl group while peak 2 around 7.0 ppm relates to proton in benzene ring. Peak 3 at 5.4 ppm and peak 4 around 3.4 ppm correspond to protons aside oxygen atom with different chemical environment. For PC, peak 5 and peak 6 locating at 4.0~5.0 ppm relate to proton aside oxygen atom and peak 7 at 1.5 ppm relates to proton in methyl group. After hydroxyalkylation reaction, the complete disappearance of peak 1 indicates that the phenol hydroxyl group has been completely reacted. The significantly decreased intensity of peak 8 suggests that a large number of aliphatic structures are introduced on TA. The emerging peak 9 (3.5~5.2 ppm), peak 10 (2.5~3.0 ppm) and peak 11 (0.9~1.6 ppm) for mTA corresponds to proton aside oxygen atom, proton in aliphatic hydroxyl group and proton in methyl group respectively, further demonstrating the successful graft of isopropanol oligomers with terminal hydroxyls. The average units per chain is calculated by comparing the integrals of methyl and aliphatic hydroxyl according to equation (2):

$$\text{average units per chain} = I_{0.8-1.6 \text{ ppm}}/3I_{2.5-2.8 \text{ ppm}} \quad (2)$$

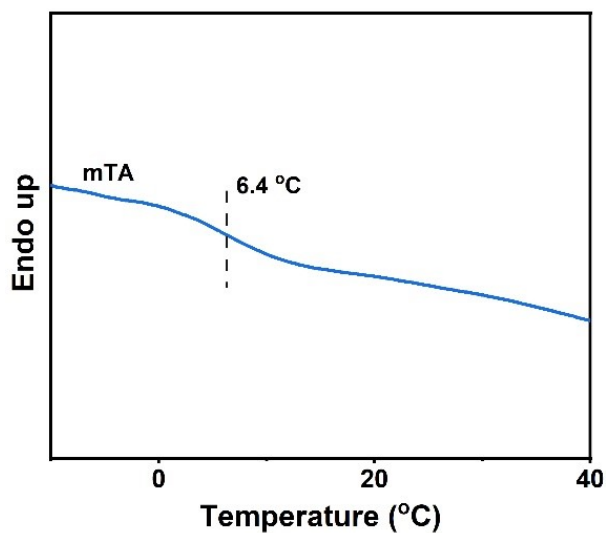
where  $I_{0.8-1.6 \text{ ppm}}/3$  and  $I_{2.5-2.8 \text{ ppm}}$  represent the content of methyl and hydroxyl respectively. The

calculated average units per chain of the mTA is 6.8 and calculated number-average molecular weight is 11561 g/mol.

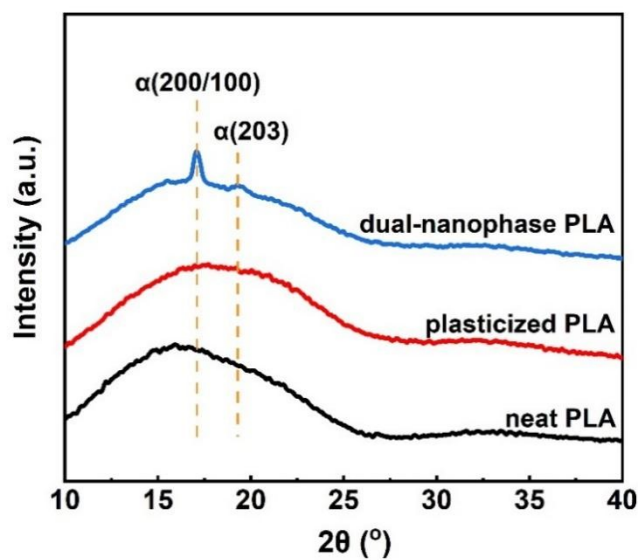


**Figure S2.** FTIR spectra of TA, PC and mTA.

For mTA, the peaks at 2800~3000  $\text{cm}^{-1}$  correspond to the stretching vibration peaks of methyl and methylene groups, demonstrating the existence of plentiful aliphatic structures in mTA. In addition, the strong peak at 1108  $\text{cm}^{-1}$  indicates the presence of a large number of ether bonds in mTA. Moreover, the strong peak at 3435  $\text{cm}^{-1}$  belonging to the stretching vibration peak of OH verifies the existence of abundant hydroxyl groups in mTA. Notably, the wavenumber of OH absorption peak in mTA is quite different from that of phenolic hydroxyl group in TA, suggesting that the hydroxyl group in mTA should be aliphatic hydroxyl group. Besides, for PC, the peak at 1788  $\text{cm}^{-1}$  corresponds to the stretching vibration peaks of carbonyl in carbonate ester. The disappearance of the peak at 1788  $\text{cm}^{-1}$  indicates the complete removing of carbonate ester. These results convincingly indicate the successful grafting of hydroxy-terminated isopropanol oligomers onto TA.



**Figure S3.** The second heating curve of mTA in DSC. A  $T_g$  of 6.4 °C is shown for the as-prepared mTA.



**Figure S4.** XRD spectra of neat PLA, plasticized PLA and dual-nanophase PLA

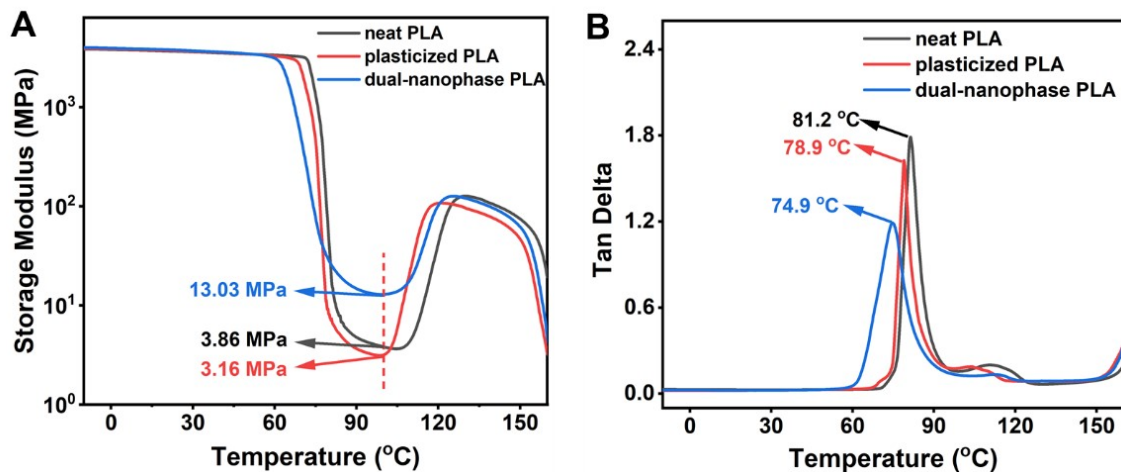
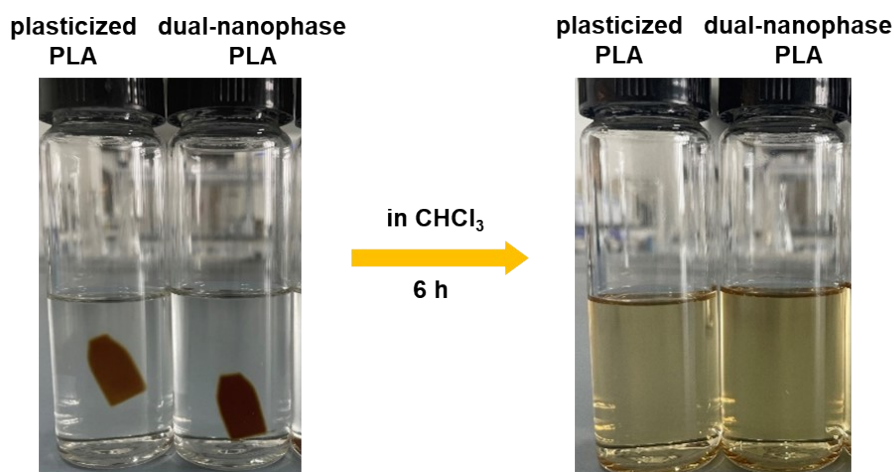


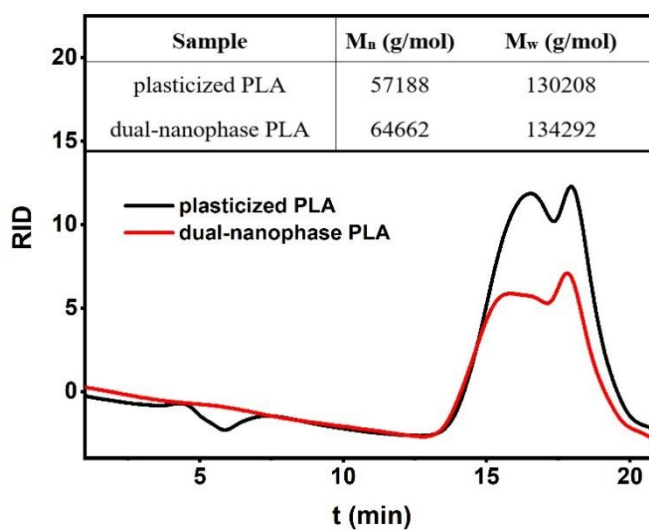
Figure S5. The dependence of storage modulus (A) and tan delta (B) on temperature of the neat PLA, the plasticized PLA and the dual-nanophase PLA.



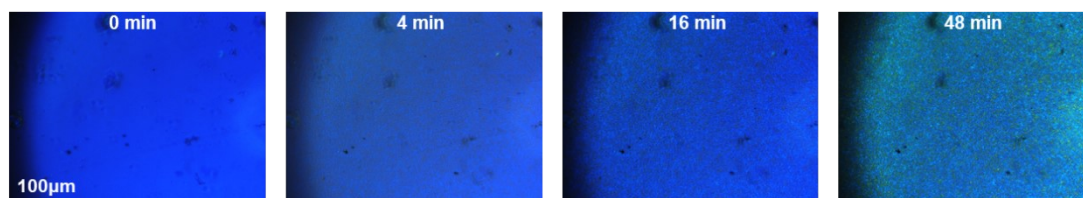
Figure S6. The surface of dual-nanophase PLA. The clean and uniform surface indicates that no plasticizer has migrated out during annealing.



**Figure S7.** Real pictures of the plasticized PLA and the dual-nanophase PLA before and after dissolution in  $\text{CHCl}_3$ . The solubility indicates that no chemical crosslinking occurs during annealing.



**Figure S8.** The GPC traces of plasticized PLA and dual-nanophase PLA.



**Figure S9.** Polarized optical micrographs of neat PLA annealed at  $100\text{ }^\circ\text{C}$ .



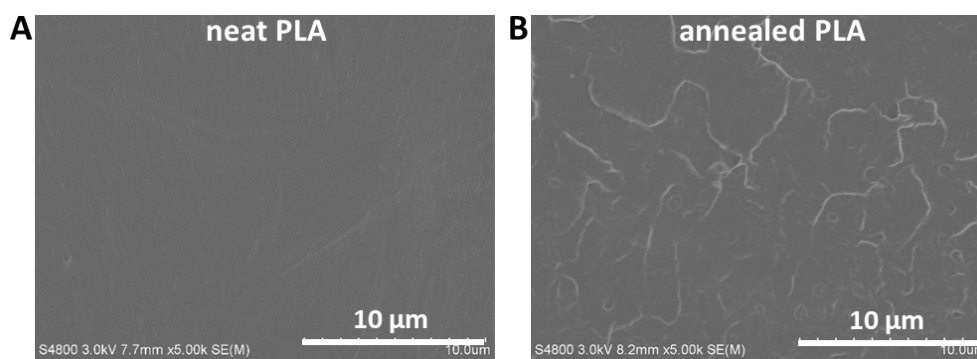


Figure S10. SEM images of neat PLA (A) and annealed PLA (B).

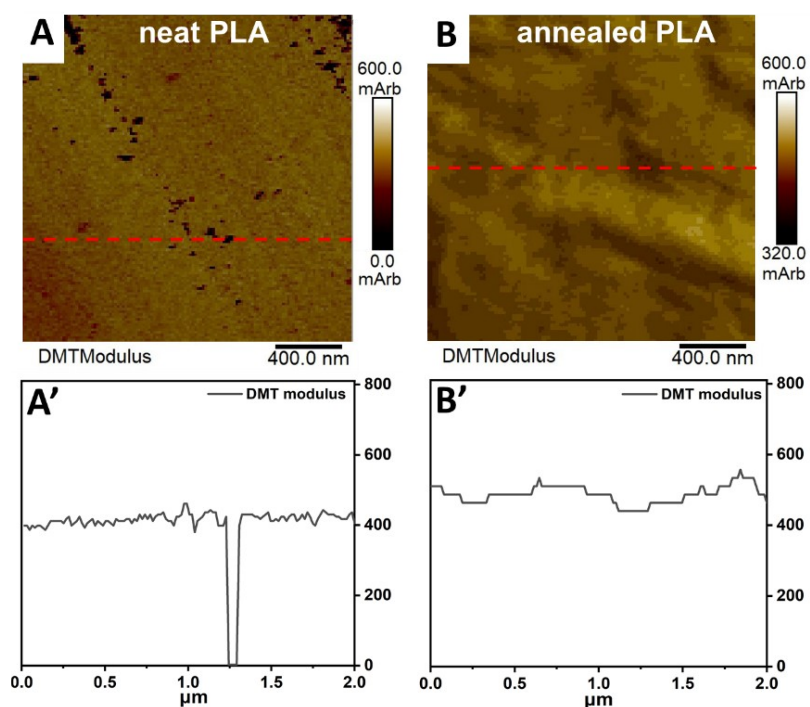


Figure S11. The DMT modulus maps of the neat PLA (A, A') and the annealed PLA (B, B')

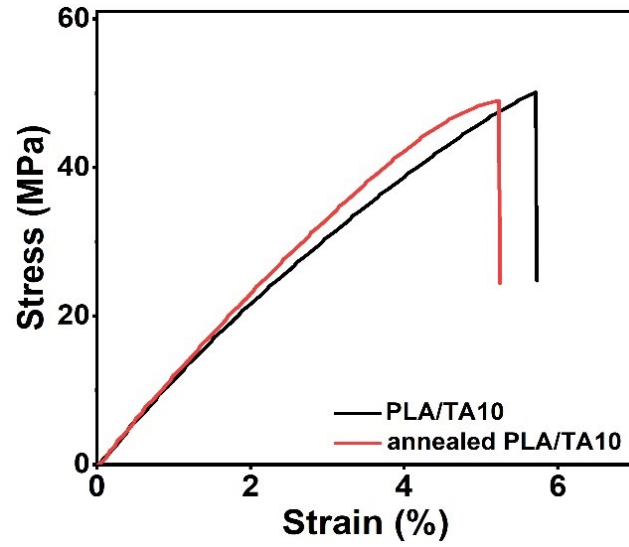


Figure S12. Stress-strain curves of PLA/TA10 and annealed PLA/TA10. The annealing temperature is 100 °C, and the annealing time is 4 min.



Figure S13. The real picture of tensile fractured PLA.



Figure S14. The real picture of tensile fractured annealed PLA.

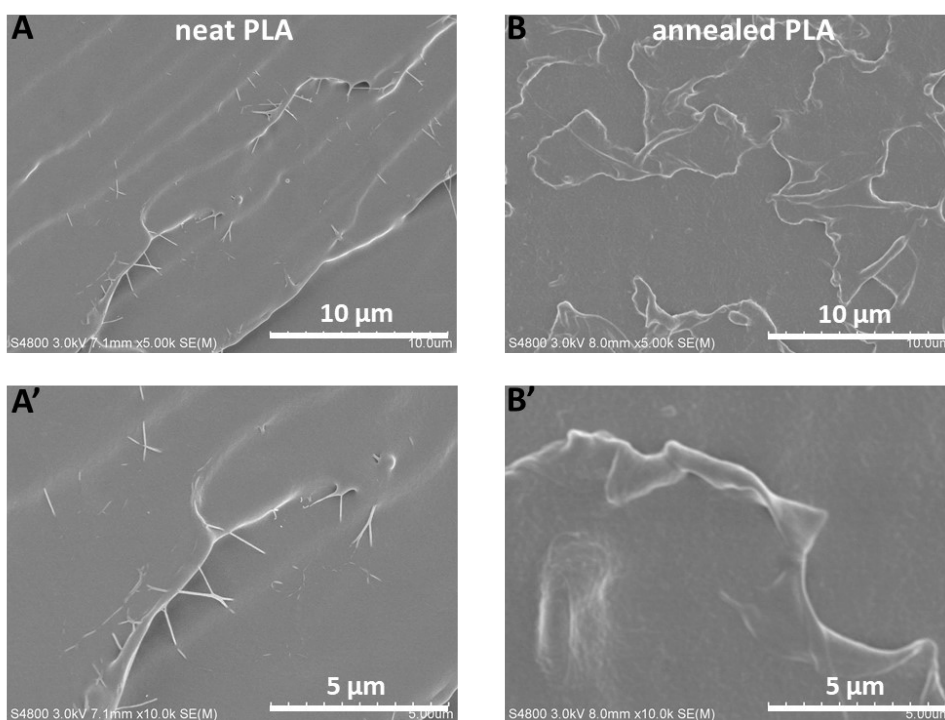


Figure S15. SEM images of tensile fractured neat PLA (A, A') and annealed PLA (B, B')

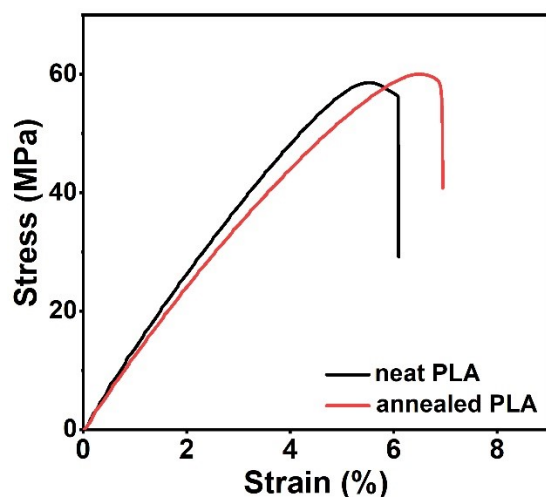


Figure S16. Stress-strain curves of neat PLA and annealed PLA.

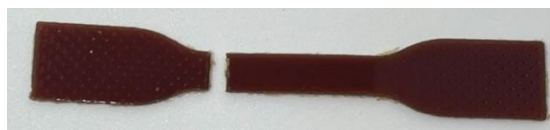


Figure S17. The real picture of tensile fractured plasticized PLA.



Figure S18. The real picture of tensile fractured dual-nanophase PLA.

**Table S1.** Detailed mechanical properties of neat PLA, plasticized PLA and dual-nanophase PLA.

Sample	Young's Modulus (MPa)	Yield Strength (MPa)	Break Strength (MPa)	Elongation at Break (%)	Toughness (MJ/m <sup>3</sup> )
neat PLA	1515±59	56.7±3.4	48.9±3.2	5.8±0.4	1.4±0.1
plasticized PLA	1551±71	57.6±3.9	35.3±2.7	20.6±3.5	7.8±0.7
dual-nanophase PLA	1879±84	69.1±4.4	41.7±2.2	279.1±15.5	115.2±10.3

