

Cellulose Nanocrystals-mediated Phase Morphology of PLLA/TPU Blends for 3D Printing

Xiao Wu^a, Yun-Xiao Liu^a, Hai-Peng Wu^a, Hao Wu^a, Hai-Jun Wang^b, Yong-Xin Duan^a, and Jian-Ming Zhang^{a*}

^a Key Laboratory of Rubber-Plastics, Ministry of Education/Shandong Provincial Key Laboratory of Rubber-plastics, Qingdao University of Science & Technology, Qingdao 266042, China

^b Shaanxi University of Science and Technology, Xi'an 710021, China

Electronic Supplementary Information

Abstract Incorporation of nanoparticles into polymer blend to obtain finely dispersed morphology has been considered as an effective strategy to prepare nanocomposites. Owing to the renewable and degradable characters, cellulose nanocrystals (CNCs) have been proposed to tailor the phase morphology of poly(L-lactic acid) (PLLA) blend for producing high-performance fused deposition modeling (FDM) consumables. However, the main challenge associated with the ternary systems is the dispersion of the highly hydrophilic CNCs in non-polar PLLA blend by industrial melt blending without involving solution. Herein, with poly(vinyl acetate) (PVAc) modified CNCs powder (a mixture of PVAc grafted from CNCs and PVAc homopolymer latex), the selective dispersion of CNCs in PLLA has been achieved by simple melt processing of PLLA/TPU (polyether polyurethane)/CNCs blend. This results in the ultra-fine TPU droplets at nanoscale in PLLA and improves the melt processability of composites in FDM due to the decreased viscosity ratio of the dispersed/matrix and the enhanced melt elasticity of PLLA. Combined with the intensive shear and continuous stretch effect during FDM, aligned TPU nanofibers (TNFs) were *in situ* formed along the elongational flow direction during deposition, which in turn contributed to the improvement of PLLA/TPU/CNCs with 5 wt% filler loading in tensile ductility by 418%, inter-layer adhesion strength and notched impact toughness by 261% and 210%, respectively, as well as achieved good dimensional accuracy and very fine surface quality.

Keywords Poly(L-lactic acid) blend; Cellulose nanocrystals; Phase morphology tailoring; 3D printing; Rheo-viscoelastic properties

Citation: Wu, X.; Liu, Y. X.; Wu, H. P.; Wu, H.; Wang, H. J.; Duan, Y. X.; Zhang, J. M. Cellulose nanocrystals-mediated phase morphology of PLLA/TPU blends for 3D printing. *Chinese J. Polym. Sci.* 2022, 40, 299–309.

INTRODUCTION

With advances in materials and technology, fused deposition modeling (FDM) is shifting from manufacturing exhibition models to producing structural parts.^[1] Poly(L-lactic acid) (PLLA) is known as one of the most promising FDM consumables for its low melting point, little awful odour, no toxic fumes, sound biocompatibility and lower coefficient of thermal expansion.^[2] However, the limited mechanical strength, the inferior surface quality and dimensional accuracy of PLLA parts limit the final application.^[1–4] Moreover, the adhesion quality and melt processability of PLLA are also unqualified because of its poor shear and extensional properties.^[4,5] All of these are related to the rheological viscoelastic properties, slow crystallization rate and brittleness of PLLA. To overcome the intrinsic drawbacks existing in PLLA, blending different polymers with complementary properties into PLLA, such as thermoplastic polyurethane (TPU), natural rubber, is the most commonly used

method.^[6–8] Whereas, the addition of nanoparticles within PLLA blend could further modify the overall properties of blend nanocomposites, which strongly depends on the final morphology and interfacial properties among the components.^[9,10]

Because of the interfacial interactions, nanoparticles could localize in one of the two phases or at the interface of both polymers. Therefore, the final properties could be influenced by series of parameters including the locations of the nanoparticles and the viscoelastic property of the whole blend. The wetting coefficient is a thermodynamic approach to predicting where the nanoparticles could be localized.^[11] Besides, the polymers rheological properties (e.g., viscosity ratio) and the melt viscoelasticity could determine the localization of nanoparticles *via* kinetics mechanism.^[9,12,13] In turn, the rheological and viscoelastic properties of the whole composites could also be influenced differently, which lies in the selective localization of the nanoparticles. These variations could also further affect the eventual morphology structure or characteristics of the blend nanocomposites.

Cellulose nanocrystals (CNCs), obtained from the biomass and known for their superior mechanical properties, large sur-

* Corresponding author, E-mail: zjm@qust.edu.cn

Received October 5, 2021; Accepted November 10, 2021; Published online January 11, 2022

face area, high aspect ratio, low cost, low density and abundance, are the promising candidates for generating new materials. However, CNCs are normally obtained as a stable aqueous suspension,^[14] the major challenge of which is their dispersion within the non-polar polymer matrix *via* direct melt blending. So far, only a few studies have been conducted on the incorporation of CNCs into polymer blend systems. Bitinis *et al.* carried out studies on the selective location of CNCs-g-PLLA in PLLA phase for the immiscible PLLA/natural rubber (NR) blends, which proved to reduce the size of NR droplets *via* a combination of casting and extrusion.^[15] In another study, the addition of CNCs masterbatch pellets enhanced the thermal stability and melt processability of PLLA/PHB blends.^[16] Heshmati *et al.* revealed the incorporation of PEO-coated CNCs in PLLA/PA11 blends.^[17] In addition, the selective localization of CNCs in PLLA influenced the viscoelastic properties of the system (a retarded relaxation of PLLA molecular chains), which in turn resulted in the achievement of finer co-continuous morphology of blends.

Recently, our group has developed a one-pot water-based method to synthesize the PVAc modified CNCs with CAN as initiator.^[18] After the hydrophobic modification, the self-precipitated powder in aqueous containing the mixture of CNCs grafted by PVAc and PVAc homopolymer particles (for convenience, the mixture of CNCs-g-PVAc/PVAc was coded as CNCs-PVAc) was obtained, which showed great prospect for low-cost modification and large-scale production. Herein, we focus on the role of CNCs-PVAc in tailoring the phase morphology of PLLA/TPU blend by melt processing and evaluate the potential of PLLA/TPU/CNCs nanocomposites on fabricating high performance 3D printing parts. The selective location of CNCs-PVAc, phase morphology, the melt processability and inter-fuse adhesion in FDM have been explored systematically, with the expectation of improving the mechanical strength, dimension accuracy and surface roughness of FDM parts for end applications. Finally, the relationship of location-structure-rheology-property in FDM has also been demonstrated.

EXPERIMENTAL

Materials

PLLA (110, with a density of 1.25 g/cm³) was supplied by Zhejiang Haizheng Biomaterials Co., Ltd. TPU (K-2685A) with a density of 1.21 g/cm³ was purchased from Shandong Kolemey Industrial Co., Ltd., China. Cotton pulp (DP=600) was supplied by Silver Hawk Co., Ltd. (Gaomi, China). Ammonium persulfate (APS, 99%) with analytical grade was purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Deionized water was used for all experiments. Vinyl acetate (VAc) and cerium ammonium nitrate (CAN) were purchased from Aladdin Chemical Reagent Corp.

Sample Fabrication

Preparation of CNCs and CNCs-PVAc

The CNCs were first prepared by the ammonium persulfate (APS) method according to our previous report and then modified by PVAc.^[19] More details of the above processes are shown in the electronic supplementary information (ESI). Only the results are presented here. The amounts of grafted and

homopolymerized PVAc are about 10% and 90%, respectively. The weight average molecular weight (M_w) and polydispersity index (PDI) of the PVA (from the grafted PVAc) were 1.48×10^5 g/mol and 1.97, respectively, and the corresponding values of homopolymerized PVAc were 2.18×10^5 g/mol and 10.9, respectively.

Preparation of PLLA/TPU/CNCs

For the preparation of PLLA/TPU/CNCs-PVAc, PLLA, TPU pellets and CNCs-PVAc powder were dried at 60 °C overnight under vacuum conditions. Then, the melt blend was carried out at 175 °C in HAAKE rheometer (HAAKE Polylos, Bruker) at a rotation rate of 60 r/min. The weight ratio of PLLA/TPU was fixed at 90/10 and the loadings of CNCs-PVAc in PLLA/TPU were set to be 0 wt%, 1 wt%, 3 wt%, 5 wt%, 7 wt%, and 9 wt%. The time of melt compounding was set to be 6 min, during which PLLA and TPU were first added into HAAKE rheometer, and then CNCs-PVAc powder was put into the mixer after 120 s. The as-prepared blends are designated as PTC_x, where the first P is PLLA, T is TPU, C is CNCs-PVAc, and x stands for the loading of CNCs-PVAc. Neat PLLA used as a reference was treated following the same procedure. Specially, in order to investigate the effect of selective location of CNCs on phase morphology and melt processability of the system, PLLA/CNCs-PVAc and TPU/CNCs-PVAc binary blends with different CNCs loadings were also prepared. For simplification, the obtained PLLA/CNCs-PVAc and TPU/CNCs-PVAc composites were designated as PCP_x and TCP_x, respectively, where the loading of CNCs-PVAc in PCP is approximate to that in PTC. And TCP with only one loading of CNCs-PVAc at 5 wt% was prepared to illustrate the effect of CNCs on TPU. All the above composites were cut into chunky pieces and used for the further preparation of FDM filaments.

Fabrication of PLLA and PTC filaments

The various granules prepared above were extruded at 165–175 °C through a single screw extruder (WSJXT-12, Shanghai Xinshuo precision machinery Co., Ltd., China) with a screw speed of 15 r/min to fabricate filaments for FDM. In this process, the pulling speed was adjusted and a vernier caliper was used to obtain filaments with a final diameter of 1.75 ± 0.05 mm.

FDM Process

First, a 3D object was created by Computer-Aided Design (CAD) software, and converted into the standard format of STL (Standard Tessellation Language). Then, the file was imported into slicing software of Simplify 3D to slice the object in different layers with different printing parameters as listed in Table 1 (prior to the confirmation of printing temperature, the thermal properties of PTC composites were tested first to clarify the influence of CNCs-PVAc on the glass transition temperature and melting point of PTC, as shown in Fig. S3 in ESI). Finally, the file obtained from the slicing software was transferred to a 3D printer (Y6018PLUS, Shenzhen Juying, China) to print the final objects. All samples are printed in accordance with the standard ISO/ASTM 5291:2013 (Standard Terminology for Additive Manufacturing-Coordinate Systems and Test Methodology).

Characterizations

Contact angle measurements were carried out at room temperature to calculate the surface tension of all the components. The measurements were conducted on a drop shape analysis system CA100C (Shanghai Innuo Precision

Table 1 3D printing parameters of PLLA and PTC filaments.

Parameter	Value
Nozzle diameter	0.4 mm
Infill percentage	100%
Layer height	0.3 mm
Printing temperature	175 °C
Printing speed	20 mm/s
Infill angle offsets	45°/−45°
Fill pattern	Rectilinear
Heat bed temperature	60 °C
Build direction	Flat/Up-right

Instruments Co. Ltd.) using the compression-molded sheets of PLLA, TPU and CNCs-PVAc. Each sample was measured for five times to obtain the average value of contact angles. The probe liquids were distilled water (H₂O) and methylene iodide (CH₂I₂).

Scanning electron microscopy (SEM) characterization was performed with a JSM-7500F field emission SEM (JEOL, Japan) at an accelerating voltage of 3–5 kV. The samples were sputter-coated with gold before SEM observations. Besides, the filaments were initially immersed in liquid nitrogen for 10 min before quick fracture.

Capillary rheology measurements were carried out on a high-pressure capillary rheometer (Rosand RH7D, Malvern Instruments Co., UK). The diameter is 1 mm and the length to diameter ratio is 16, which is long enough to ensure that the results obtained were independent of capillary geometry. Measurements were conducted at 175 °C, corresponding to the printing temperature. Besides, the shear rates vary from 100 s^{−1} to 10000 s^{−1}.

The small amplitude oscillatory shear (SAOS) experiments were performed on a TA ARES G2 (TA Instruments Co., USA) in the nitrogen atmosphere to determine the zero shear viscosity of PLLA and PTC composites. The hot-pressed samples were obtained with a diameter of ca. 25 mm and thickness of ca. 2 mm. The dynamic frequency sweeps were conducted with the fixed strain of 1% at 175 °C, within a range from 0.0628 rad/s to 628 rad/s.

Tensile properties were measured with a universal testing machine (REOLL 2005, ZWICK). The dumbbell-shaped specimens were prepared with the width of ca. 4 mm and thickness of ca. 2 mm. The gauge distance was set as 25 mm and a

cross-head speed of 2 mm/min was used. Area under stress-strain curve was considered as tensile ductility of the composites. Prior to the mechanical testing, all specimens were conditioned for 48 h with 50% relative humidity at 23 °C according to ISO 527.

Izod and Notched impact test were performed by GT-2045-MDN and GT-7045-MDH impact devices, respectively. Impact test samples were printed with a thickness of ca. 4 mm, a width of ca. 10 mm and a notch depth of 2 mm. To ensure the reliability of data, 8 specimens were prepared for each composition.

Nikon SMZ 1500 stereoscopic microscope was applied to observe the surface quality of mono-layer tensile samples by FDM, with the magnifications at 10× and 50×.

Surface roughness (R_a) of FDM cylinders (Φ15 mm × 15 mm) in Z-axis direction was measured using surface roughness tester (3D Measuring Laser Microscope OLS5000). Measurement of R_a was taken for three times at different counters so as to reduce error. The selection size for the test is 2550 μm × 2569 μm.

RESULTS AND DISCUSSION

Filament Fabrication and Phase Morphology

The filament with high quality is the prerequisite for FDM. However, it is a bit difficult for neat PLLA with low melt strength to fabricate filament with uniform appearance under shear and extension effect during extrusion. Herein, ternary blend of PLLA/TPU/CNCs (PTC) was first melt-processed in HAAKE rheometer and then extruded by single screw extruder to fabricate FDM filaments, expecting a refined phase morphology to improve the rheological viscoelastic properties of PLLA.

As shown in Fig. 1(a), in contrast to the uneven diameter of neat PLLA filament, PTC filaments exhibit relatively uniform appearance. This phenomenon is closely related to the improved rheo-viscoelastic properties of PTC, which will be discussed later in detail.

Phase Morphology

SEM was used to characterize the microstructure of PTC blends with different loadings of CNCs-PVAc, the results of which are presented in Figs. 1(b)–1(e). Fig. 1(b) exhibits a typical sea-island

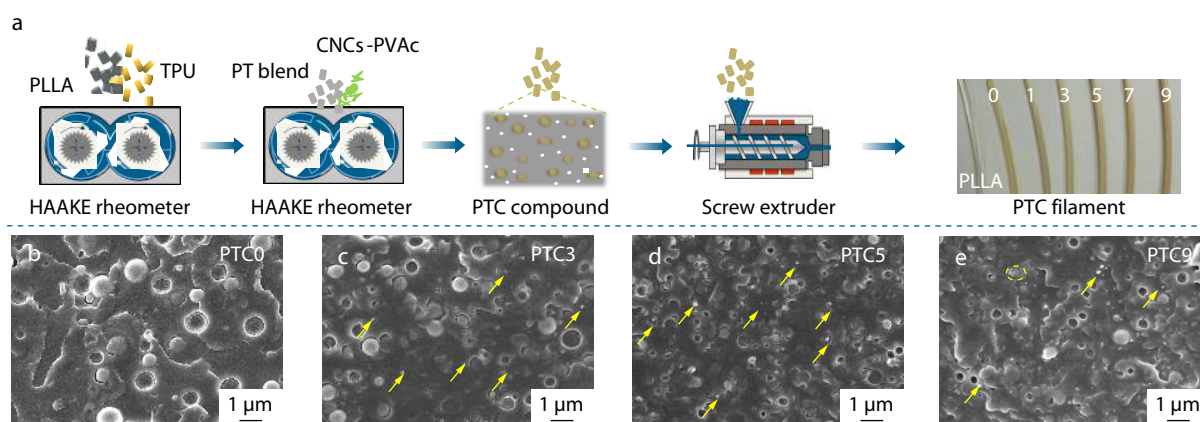


Fig. 1 (a) Schematic illustration of the filament fabrication process of PLLA and PTC composites; (b–e) SEM images of the cryo-fractured surfaces of PTC filaments.

structure, namely, spherical TPU droplets randomly dispersed in continuous PLLA, which is consistent with the previous work.^[10] Sizes of these TPU droplets are around 1 μm , indicating a good compatibility between PLLA and TPU.^[20] With the increase of CNCs-PVAc, sizes of some individual TPU droplets tend to decrease (Fig. 1c). With further increase of the amount of CNCs-PVAc to 5 wt%, sizes of TPU droplets tend to further decrease to the nanoscale (Fig. 1d). Moreover, with PTC0 as a reference, CNCs-PVAc particles are almost exclusively located in PLLA of the blends with a good dispersion at nanoscale. The CNCs can be clearly observed as white dots, correlating with the transverse section of their particles, which is shown by the yellow arrows. This may be related to the loose structure of CNCs-PVAc and the good miscibility of PVAc with PLLA. Previous research has demonstrated that PLLA and PVAc were miscible in the entire composition range, with a single glass transition T_g observed for all the blends.^[21] Besides, this localization is stable over the whole range of CNCs-PVAc loading. However, once the content of CNCs-PVAc is up to 9 wt%, the agglomeration of CNCs-PVAc will occur, which is shown by the yellow circle in Fig. 1(e). The sizes of TPU droplets recover to bigger ones again. This is most probably caused by the accumulation of large amount of CNCs-PVAc in PLLA beyond its saturation concentration and their inevitable dispersion in TPU, thus leading to the increase in modulus and viscosity of TPU droplets.

Nevertheless, the resolution of SEM is generally insufficient to identify individual nanoparticles (but to identify the presence of aggregates).^[22] Because the electrical charge effects could increase the apparent cross-section of the nanorods or possible CNCs aggregates. Therefore, AFM characterization was performed for selected sample, the result of which is consistent with SEM observation, as is shown in Fig. S4 (in ESI).

Role of CNCs-PVAc in Tailoring Phase Morphology

Previous researches have shown that the change of rheological behavior of blends in terms of viscosity ratio,^[23] elasticity,^[24] or interfacial tension,^[25] is generally believed to be the most possible mechanism of phase morphology change. Here, to clarify the role of CNCs-PVAc on the phase morphology changes of PTC blends, both the thermodynamic and kinetic factors were taken into consideration.

The wetting coefficient (ω_a) is widely accepted to predict the thermodynamic equilibrium location of nanofillers in immiscible polymer blends, defined as Eq. (1):^[26]

$$\omega_a = \frac{\gamma_{\text{PLLA-CNCs}} - \gamma_{\text{TPU-CNCs}}}{\gamma_{\text{PLLA-TPU}}} \quad (1)$$

where γ is the interfacial tension between components. If $\omega > 1$, CNCs-PVAc will be localized in TPU; if $\omega < -1$, in PLLA, and if $-1 < \omega < 1$, the interface will be the preferred location of CNCs.

The interfacial tension (γ) can be calculated as follows; For materials with high surface energy the harmonic-mean equation:^[27]

$$\gamma_{12} = \gamma_1 + \gamma_2 - 4 \left(\frac{\gamma_1^d \gamma_2^d}{\gamma_1^d + \gamma_2^d} + \frac{\gamma_1^p \gamma_2^p}{\gamma_1^p + \gamma_2^p} \right) \quad (2)$$

while for materials with low surface energy the geometric-mean equation:^[28]

Table 2 Interfacial tensions and wetting coefficient (ω_a) calculated via Harmonic and Geometric mean equations.

Component couple	Harmonic mean Eq. (mN/m)	Geometric mean Eq. (mN/m)
$\gamma_{\text{CNCs-PLLA}}$	1.98	1.01
$\gamma_{\text{CNCs-TPU}}$	14.8	9.61
$\gamma_{\text{PLLA-TPU}}$	8.05	5.02

$$\gamma_{12} = \gamma_1 + \gamma_2 - 2(\sqrt{\gamma_1^d \gamma_2^d} + \sqrt{\gamma_1^p \gamma_2^p}) \quad (3)$$

where γ_i is the surface tension of component i , γ_i^d and γ_i^p are the contribution of dispersive and polar molecular interaction to the surface tension of component i , respectively.

To calculate the surface tension, the contact angle between liquid and polymer surface is first measured (Fig. S5 in ESI), and then the surface tension can be calculated according to Owen method,^[29] the results of which are listed in Table S2 (in ESI). According to Eqs. (1)–(3), the calculated values of interfacial tension γ are summarized in Table 2.

The ω_a is -1.59 and -1.71 , respectively, based on the above harmonic mean equation and the geometric mean equation. This indicates that CNCs-PVAc tends to selectively locate in PLLA, which is in good agreement with the above SEM and AFM results.

From the kinetic point of view, the dynamic viscoelasticity of single polymer nanocomposites with CNCs-PVAc is shown in Fig. 2. Fig. 2(a) shows the variation of complex viscosity (η^*) with angular frequency (ω) for PLLA and PCP composites, where the loading of CNCs-PVAc in PCP is approximate to that in PTC. And the loading of CNCs-PVAc in TCP is only one dosage of 5 wt% to illustrate the effect of CNCs-PVAc on TPU. In the graph, the η^* of both PLLA and TPU is sensitive to the addition of CNCs-PVAc. When the CNCs-PVAc content was < 5 wt%, the η^* increase of PCP was relatively slow with the increase of CNCs-PVAc. In addition, the initial complex viscosity of PLLA and PCP tended to be a constant at low frequencies ($\omega < 1$ rad/s). However, when the filler content exceeded 5 wt%, the η^* of PCP increased rapidly. To be specific, the complex viscosity of PCP10 is 1005 Pa·s, more than 4 times higher than that of neat PLLA (232 Pa·s) at the frequency of 0.1 rad/s, revealing that rheological percolation threshold of filler may occur between 5 wt% and 10 wt% of CNCs-PVAc in PLLA. Namely, CNCs-PVAc network comes into formation, resulting in long range PLLA chain relaxation being restrained. This is also consistent with the research results by Kamal *et al.*, with the following rheological features as an indication of solid-network formation initiation: (a) the sudden shortened linear viscoelastic region, (b) an upturn in the complex viscosity at low frequencies.^[29] In addition, the relationship between η^* and frequency is nonlinear, presenting a typical shear-thinning behavior. This could be attributed to the disentanglement of the polymer chains under flow.^[5,30] What's more, the formation of filler network will partly inhibit the melt flow of PLLA, weakening the shear on TPU droplets. Hence, the appropriate concentration of filler is the prerequisite to obtain the minimum TPU droplets size, e.g., 5 wt% CNCs-PVAc in this work.

Filippone *et al.* proposed that the selective location of nanofiller in one phase of blends should enhance the melt elasti-

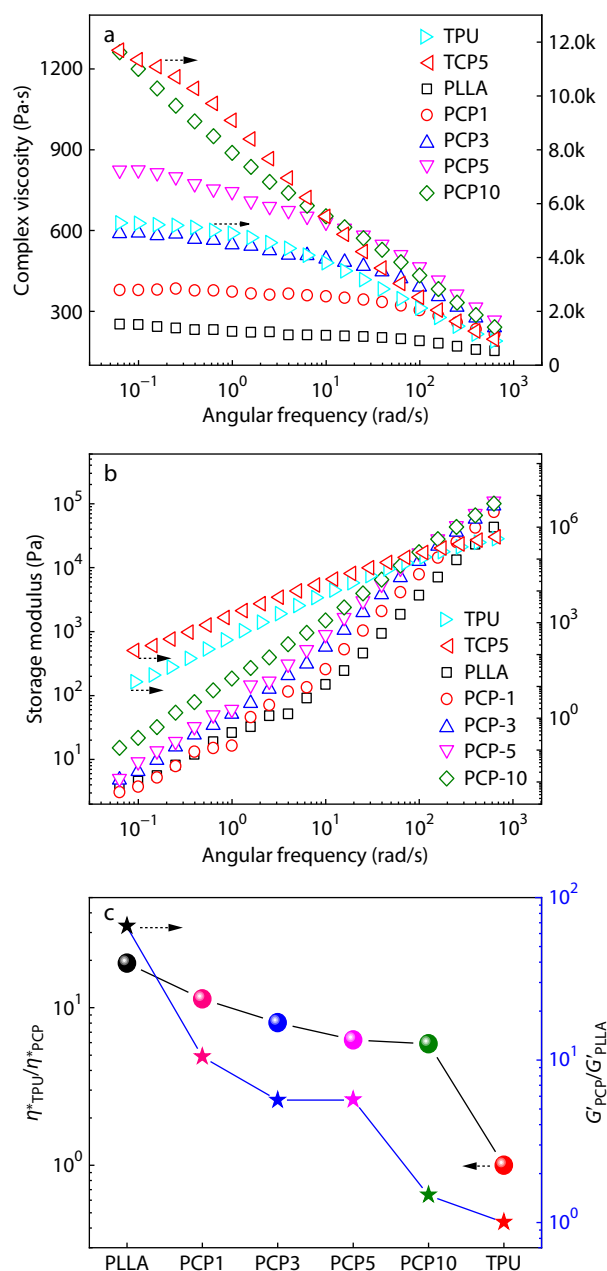


Fig. 2 The relationship of (a) the complex viscosity, (b) storage modulus versus angular frequency (ω) of PLLA/PCP (values of Y-axis on the right in (a) and (b) correspond to TPU/TCP), and (c) the values of $\eta_{TPU}^*/\eta_{PCP}^*$ and G'_{PCP}/G'_{PLLA} .

city of it.^[24] In this work, the storage modulus (G') of PCP and TCP filled with CNCs-PVAc is shown in Fig. 2(b). Clearly, with the increase of CNCs-PVAc, the G' of PCP and TCP increases progressively, which indicates an enhanced melt elasticity. For instance, the G' of PCP and TCP at 5 wt% CNCs-PVAc is 5.68 and 2.52 times greater than that of neat matrix at the frequency closest to the processing conditions, respectively (Fig. 2c). The increased G' of PCP leads to a delayed dynamic relaxation of PLLA chains in the studied frequency range, which in turn contributes to the coalescence suppression or the stability of refined TPU droplets in PTC composites, con-

sistent with the previous work.^[31] The same conclusion holds for TCP.

As we know, the viscosity ratio plays an indispensable role in tailoring phase morphology of immiscible blends. The value of $\eta_{TPU}^*/\eta_{PCP}^*$ (Fig. 2c) decreases from 19.2 to 6.25 with 5 wt% CNCs-PVAc in PLLA, which is in agreement with the refined sea-island structure of PTC in Fig. 1(d). However, when the $\eta_{TPU}^*/\eta_{PCP}^*$ of PCP10 changes from 19.2 to 5.90, no more refined TPU droplets of the system is achieved. This phenomenon is most probably caused by the agglomeration and network of CNCs-PVAc formed in PLLA discussed above, partly restricting the melt flow of PLLA and weakening the shear effect of PLLA on TPU droplets. Another possible reason is the increase in modulus and viscosity of TPU droplets because of the inevitable dispersion of CNCs in TPU, with the amount of CNCs exceeding its saturation concentration in PLLA.

In brief, combined with the thermodynamics and kinetics effects, the selective dispersion of CNCs in PLLA has been successfully achieved, leading to the most refined TPU droplets with 5 wt% CNCs-PVAc loading, which results from the decrease of viscosity ratio of TPU/PLLA and the increase of PLLA melt elasticity caused by the selective distribution of CNCs in PLLA. All these facilitate the break-up and immobilization of the dispersed TPU droplets.

Viscoelasticity of PTC for FDM Processing

The changes of phase morphology described above are bound to affect the melt viscoelasticity of PTC filaments. Viscoelastic properties of materials are highly dependent on the shear rates during processing. The shear rate involved at nozzle during FDM is available in ESI section 6.

Viscoelastic Behavior of PLLA and PTC in the Extruding Process

Filaments are first extruded through nozzle under high shear. Thus, appropriate viscosity (η) and viscoelasticity are needed to ensure the smooth liquefaction process without unsteady flow.^[27] The apparent viscosity (η_a) versus shear rate ($\dot{\gamma}$) of PLLA and PTC filaments with different CNCs-PVAc loadings is shown in Fig. 3. As shown in Fig. 3(a), with the increase of CNCs-PVAc, the η_a of PTC increases first and then decreases, which is consistent with the agglomerates of CNCs in PTC9, where polymer chains entanglement between matrix and CNCs-PVAc could be suppressed to some extent. In addition, it presents a decrease of η_a with the increasing shear rates, indicating a notable shear-thinning behavior. This can be attributed to the disentanglement of the polymer chains under flow.^[5,27]

Furthermore, Power Law Model is employed to calculate the non-Newtonian index (n), as is displayed:^[5,32] $\eta = k \cdot \dot{\gamma}^{(n-1)}$, where η is the apparent viscosity, $\dot{\gamma}$ is the shear rates, n is the non-Newtonian index, and k is the consistency index.

As is shown in Fig. 3(b), all the n values of PLLA and PTC are below 1, showing the characteristic of pseudo-plastic fluid. The smaller the n is, the faster the viscosity will drop, which is conducive to the stable and smooth extrusion of melt from nozzle.^[27] This provides an effective way to control the viscosity of PTC for FDM by tailoring the loading and location of CNCs-PVAc. With PTC5 presenting the minimum n value, it can be inferred that subsequent extrusion of filament PTC5 will be the most stable.

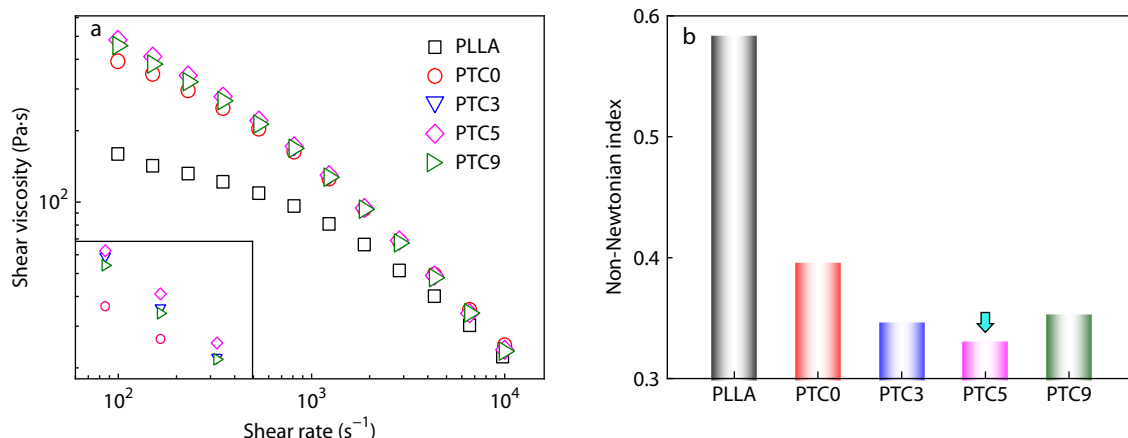


Fig. 3 The apparent viscosity versus shear rates (a), non-Newtonian index (b) of PLLA and PTC composites with different CNCs-PVAc loadings.

Viscoelastic Behavior of PLLA and PTC in the Welding Process

During FDM deposition, fuses extruded by nozzle are not subjected to shear force in the welding process, leading to a free interface,^[30] which is different from the traditional injection molding. Therefore, zero shear viscosity (η_0) is a vital parameter affecting the inter-fuse adhesion.

Fig. 4(a) compares complex viscosity versus angular frequency of PLLA and PTC by SAOS measurement. In general, the complex viscosity of blends increases with the addition of TPU and CNCs-PVAc owing to the interaction between matrix and the additive components. In the low-frequency range, both PLLA and its blends exhibit a Newtonian plateau except PTC9, whereas they demonstrate typical shear thinning in the high-frequency range. Moreover, with the increase of CNCs-PVAc, the shear thinning behavior becomes more significant, representing a typical characteristic of the pseudoplastic fluid behavior.

For instance, the complex viscosity of PTC9 is 2060 Pa·s, which is 20 times higher than 99.0 Pa·s of neat PLLA's at the angular frequency of 0.1 rad/s. This mainly lies in the fact that rheological percolation threshold occurs between 5 wt% and 10 wt% of CNCs-PVAc in PLLA. Namely, nanoparticles network of CNCs-PVAc comes into formation, resulting in long range PLLA chain relaxation being restrained. Thus, the typical shear thinning behavior of PTC9 is due to not only the gradual disentanglement of highly physically entangled molecules of PLLA/TPU but also the destruction of CNCs-PVAc network.

To calculate η_0 of PLLA and PTC, Cox-Merz rule is employed here to transform the relationship between complex viscosity and angular frequency (Fig. 4a) into shear viscosity under steady state versus shear rate.^[29] Furthermore, when complex viscosity at low frequency presents a linear plateau, Cross-Williamson model is used to mathematically obtain the η_0 of PLLA and PTC by curves fitting, given as follows:^[5]

$$\frac{\eta - \eta_\infty}{\eta_0 - \eta_\infty} = \frac{1}{1 + \lambda \dot{\gamma}^m} \quad (4)$$

where η and $\dot{\gamma}$ are viscosity and shear rate, respectively. λ , m , η_∞ and η_0 are relaxation time, shear thinning behavior parameter, viscosity at infinite and zero shear rate, respectively. In this model, with experimental data being fitted, the η_0 of PLLA and

PTC (except PTC9) could be disclosed, as is vividly presented in Fig. 4(b).

The η_0 increases significantly with the increasing CNCs, *e.g.*, the η_0 of PTC5 increases to 965 Pa·s, compared with 95.7 Pa·s of neat PLLA's. Moreover, along with η_0 , both storage modulus (G') and loss modulus (G'') also show evident increase, as shown in Fig. 4(c) or 4(d). This is due to the extended relaxation time of PLLA macromolecular chains, resulting from the selective dispersion of CNCs-PVAc in PLLA and the subsequent refined phase morphology (namely, larger interphase area) of PTC. In addition, G' relates to elasticity deformation and G'' relates to viscosity of PTC fuses, both of which are associated with the contact and coalescence of fuses. What's more, G'' is greater than G' , indicating that the viscosity of PLLA and PTC is greater than the elasticity, which is beneficial to inter-fuse adhesion during welding.

Micro-structure and Surface Roughness of FDM Samples

The change of the above viscoelasticity is closely related to the interfacial adhesion and surface roughness of PTC parts. Herein, surface morphology (of mono-layer tensile specimens) and roughness (of FDM cylinders in Z-axis direction) of PLLA and PTC samples were observed. As is illustrated in Figs. 5(a) and 5(b), voids and narrow gaps (shown by the yellow arrows) can be clearly observed in the FDM samples, thus reducing the contact area between fuses. This may be because of the nonuniform filament, low η_0 (Fig. 4b) or thermal shrinkage of PLLA and PTC0 fuses out of nozzle. With the addition of CNCs-PVAc, gaps or voids gradually disappeared and fuse quality was obviously improved (Fig. 5c/c₁), consistent with the improved viscoelasticity of PTC fuses in Figs. 3 and 4, resulting in the good adhesion between fuses. To be specific, fuses of PTC5 presented the best quality and possessed the uniform appearance (Fig. 5d/d₁), with the chance of more contact or coalescence, as well as physical and mechanical property improvement of parts. This could be due to the most stable extrusion corresponding to the smallest n value (Fig. 3b), moderate η_0 and modulus (Fig. 4b) of PTC5. As the CNCs-PVAc further increased, gaps reproduced between adjacent fuses of PTC9 (Fig. 5e/e₁), resulting in weak inter-fuse adhesion within the definite time of deposition. We proposed that it should be mainly due to the highest value of η_0 and G of PTC9 (Fig. 4), which restricted the molecular diffusion

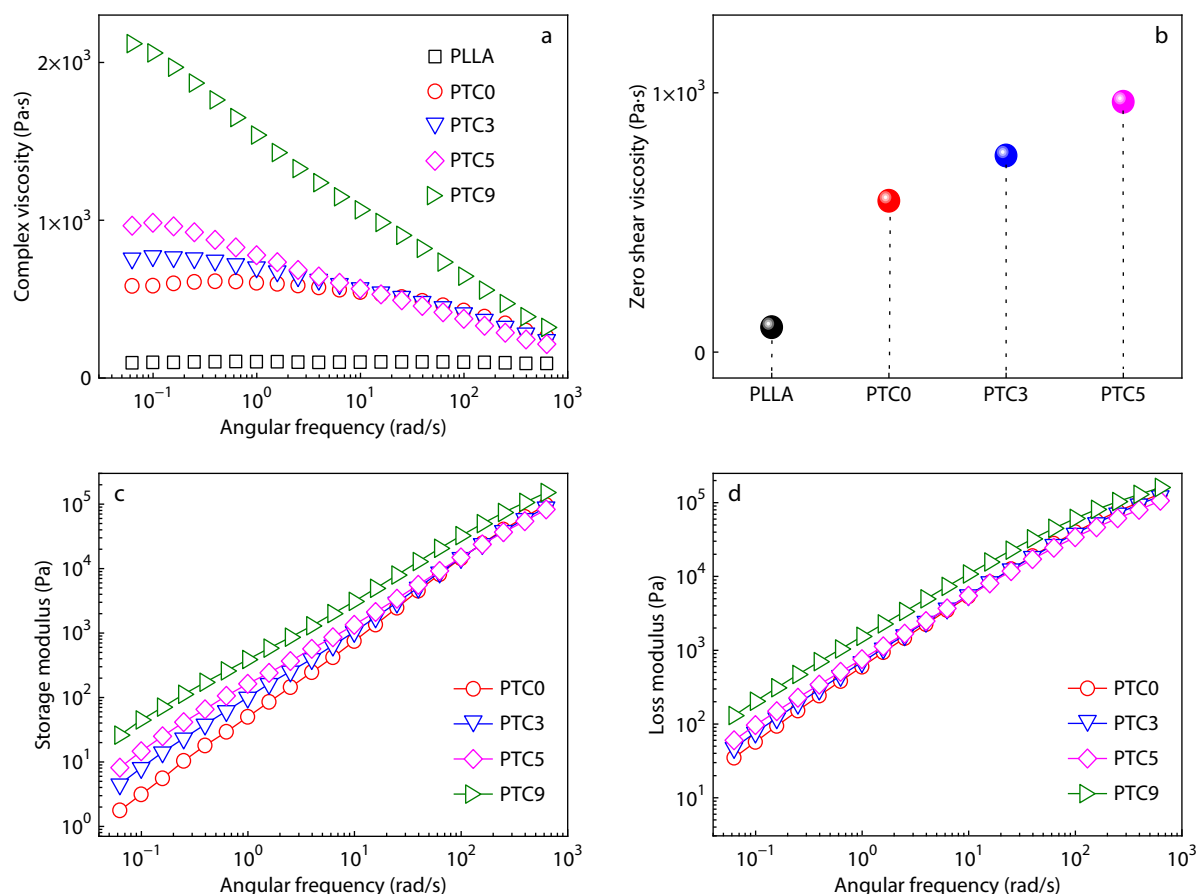


Fig. 4 The complex viscosity versus angular frequency (a), zero shear viscosity (b), storage modulus (c), and loss modulus (d) of PLLA and PTC composites.

flow and elastic deformation response of fuses at the interface, thus contributing to a possibly lower mechanical property.

The surface roughness of the final parts is critical for high-end application. In general, the horizontal surface parallel to the build plane in FDM, is the smoothest, while the vertical surface, orthogonal to the build plane, possesses the roughest surface.^[33] However, the layer thickness could not be too small owing to the diameter of extruded fuse being hundreds of micrometers. Hence, determined by the layer-by-layer binding process, the staircase in Z-axis direction is remarkable and inevitable. Durgun *et al.* have found that perpendicularly-printed specimens have the worst surface roughness (R_a) compared to horizontal parts.^[34] In addition, staircase defect is one of the main issues in FDM. So far, few researches have been done on the smooth printing of PLLA products by FDM. Figs. 5(a₂)–5(e₂) shows the results of staircase roughness of PLLA and PTC by FDM, measured by a laser surface measuring device. It can be found that a better surface roughness can be achieved by adjusting CNCs loading without changing hardware configurations. For instance, the R_a of PLLA is 238 μm , while the R_a of PTC5 decreased to 27.7 μm (Table 3). This is because the fuse extruded through nozzle is pressed between the substrate and nozzle tip. A fuse with even thickness helps to fabricate a surface with good surface roughness. However, the width of fuse is not uniform since the material was extruded improperly through the nar-

row gap (0.1 mm in this work) between nozzle and substrate, which was closely related to the viscoelasticity of composites discussed above.

Physico-mechanical Properties

Filament is heated, extruded out of nozzle and then deposited, during which it withstands a strong shear-and-dragging force along the elongational flow direction,^[35] exerting influence on the final phase morphology within FDM parts. With printed samples shown in Fig. 6(a), Izod and Notch impact tests were first performed to measure the inter-layer adhesion and toughness of PLLA and PTC parts. Then comes the tensile properties, the most common properties that have been evaluated by researchers so far, and the dimensional accuracy of FDM parts.

Impact Properties of PLLA and PTC Parts

Izod and notch samples of PLLA and PTC were impacted parallel and perpendicular to the deposition plane, respectively, contributing to the breakage of inter-layer adhesion (another reference to measure the inter-layer adhesion by tensile test^[36] has also been performed, and the result was presented in the ESI, Fig. S6) and trans-layer fuses, the results of which are illustrated in Figs. 6(b) and 6(c).

As is shown in Fig. 6(b), with the increase of CNCs-PVAc, Izod impact strength of the parts increases first, with PTC5 reaching a maximum, and then decreases. Notch impact

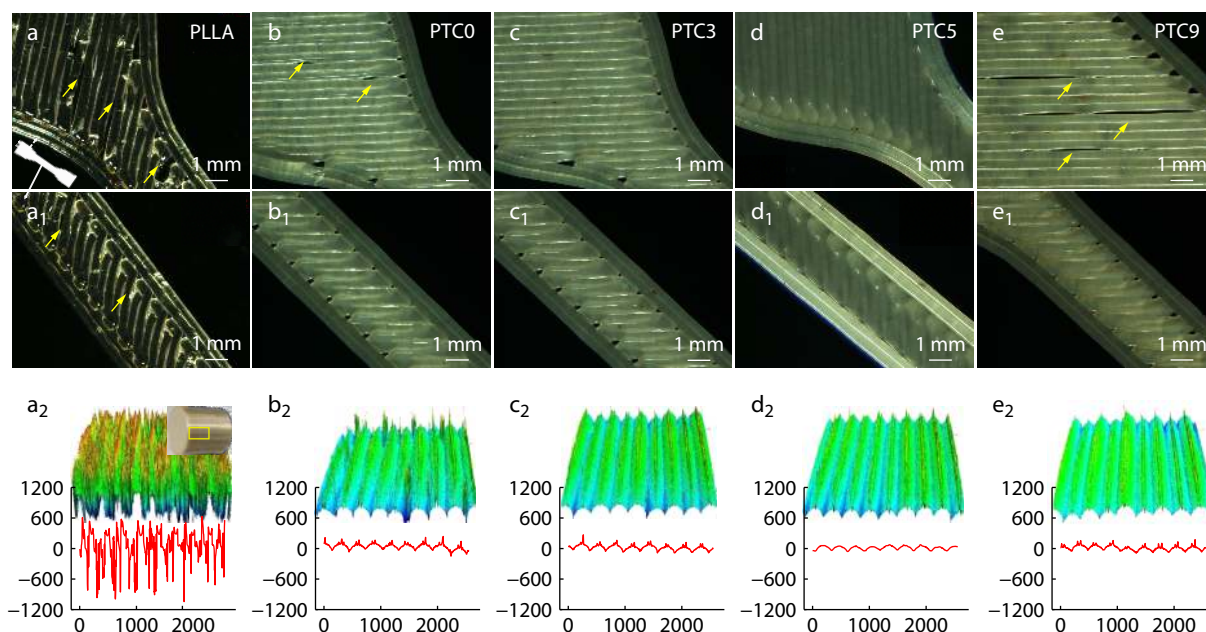


Fig. 5 Stereoscopic microscope images of monolayer tensile samples (a/a₁–e/e₁), surface roughness of cylinders in Z-axis direction (a₂–e₂) of PLLA and PTC with the selection size of 2550 $\mu\text{m} \times 2569 \mu\text{m}$ (in red).

Table 3 Surface roughness (R_a) of FDM cylinders in the Z-axis.

Sample	PLLA	PTC0	PTC3	PTC5	PTC9
Roughness R_a (μm)	238	40.4	35.0	27.7	33.7

strength shows the similar trend, Izod and notch impact strength of PTC5 are 4.97 and 2.98 kJ/m^2 , respectively, which are 261% and 210% of neat PLLA's.

Figs. 6(d)–6(h) show the fractured surface microstructure of Izod samples by SEM, with PTC5 presenting the best adhesion and relatively homogeneous section, which is consistent with the above Izod performance and stereoscopic microscope observation in Fig. 5.

With magnified images in Figs. 6(d₁)–6(h₁), it can be found that the fracture surface of PLLA is relatively smooth. Yet observing PTC0 in Fig. 6(e₁), the dispersed and orderly oriented TPU fibers were *in situ* formed, with PLLA matrix almost no deformation, suggesting that little impact energy has been consumed. This is because during printing, the nozzle and its relative movement to the platform provide the strong shear and stretch force to fuse, making the TPU droplets in PLLA undergo the intense and continuous volume stretching deformation. Then, TPU droplets connected with each other forming *in situ* aligned fibers, thus toughening the matrix.^[29,30] Furthermore, it is worth noting that the orientation amount and degree of refinement of TPU fibers increase with the increase of CNCs-PVAc. For instance, superfine TPU fibers at nanoscale (TNFs) appeared on the fractured surface with 5 wt% CNCs-PVAc, which was consistent with the minimum TPU droplets in PTC5 filament (Fig. 1e). Then the fineness of TNFs showed little decrease (Fig. 6h₁) in PTC9 because of the increasing size of TPU droplets during processing, resulting from the network of CNCs formed in PLLA and probable dispersion of CNCs-PVAc in TPU. Meanwhile, PLLA matrix underwent significant deformation, indicating that large amount of energy

have been consumed. This might be caused by the improved interfacial adhesion and compatibility between PLLA and ultrafine TPU fibers under the strong shear and stretching during FDM, which also significantly enhanced the impact strength of PTC parts.

However, in Fig. 6(j₁)–(m₁), where the impact direction is perpendicular to the deposition plane, TPU fibers cannot be detected clearly on the magnified fractured surface but typical sea-island structure, interspersed with cavity and deformed PLLA. It is worth noting that oriented TPU fibers can be partly observed on the inclined fracture surface of PTC5 fuse. Once again it proves that the orientation of TPU fibers can be observed in the direction parallel to deposition plane after impact.

Tensile Properties of PLLA and PTC Parts

The tensile strength of FDM parts can be considered as contributions from the strength of fuses and interface adhesion among fuses. Fig. 7(a) presents the tensile stress-strain curves of printed PLLA and PTC parts. Neat PLLA exhibits a typical brittle fracture behavior. The mechanical properties parameters derived from the stress-strain curves are summarized in Table S3 (in ESI). As is shown in Fig. 7(b), the addition of TPU helped improve the tensile ductility slightly, but lowered the tensile strength and modulus. With the addition of CNCs-PVAc, a considerable reinforcement was observed with distinct yield point. To be specific, PTC5 exhibits the maximum tensile properties with the strength and modulus of 40.2 and 2682 MPa, respectively, an improvement of the fracture energy by 418%, compared to those of 32.5 and 2352 MPa for neat PLLA's. Yet with further increase of CNCs, the tensile strength of PTC9 showed visible decrease, consistent with its tensile ductility. Similar trends in tensile strength for CNCs-reinforced composites were also reported elsewhere.^[20]

Fig. 7(c) shows the dimensions and the dimensional stability of printed PLLA and PTC tensile samples. It can be found

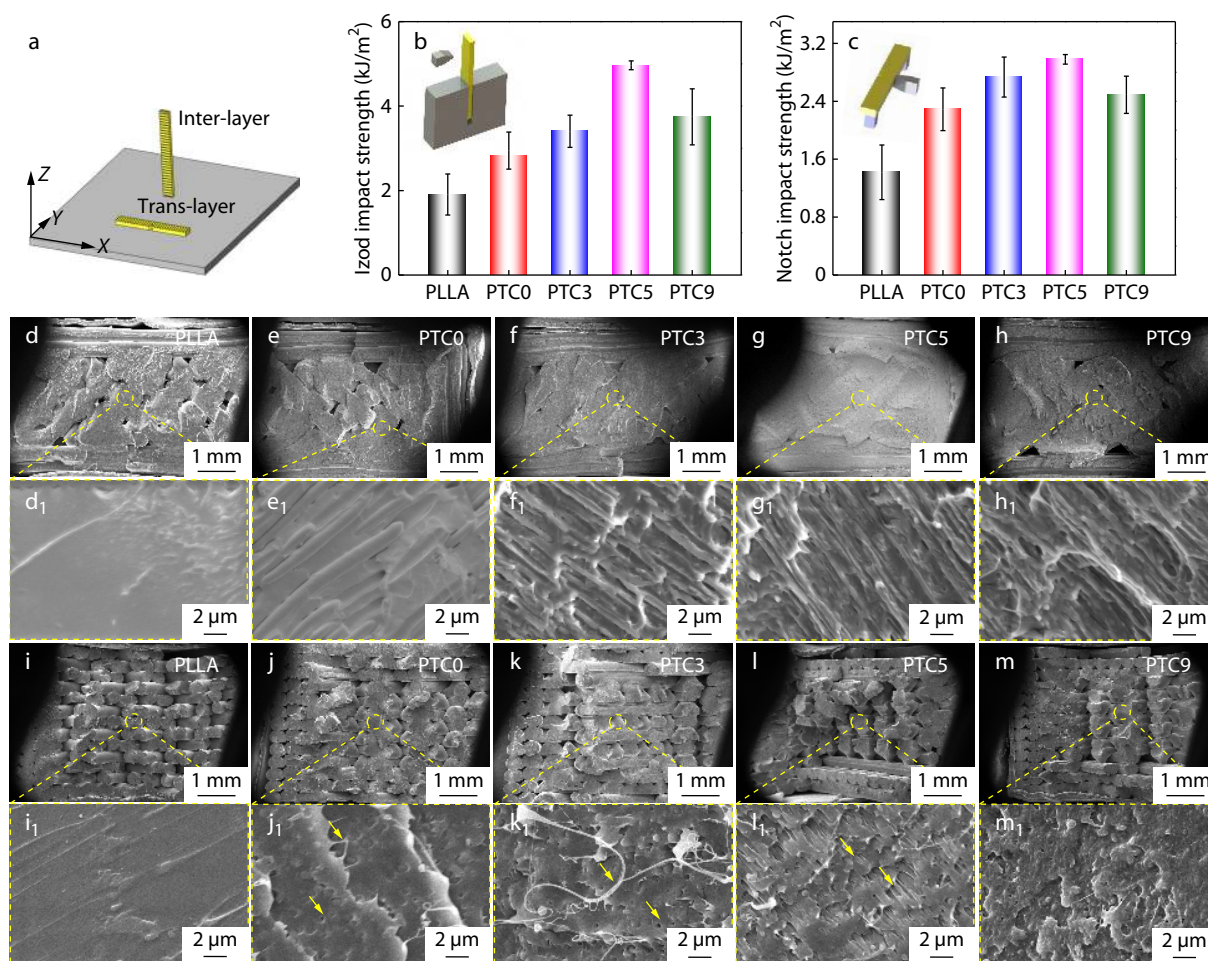


Fig. 6 The schematic illustration of printing directions (a), Izod (b) and Notch (c) impact strength, SEM fracture surface images of Izod (d/d₁–h/h₁) and Notch (i/i₁–m/m₁) of PLLA and PTC parts.

that as the CNCs loading increases, the width and thickness of PTC are increasing gradually, with the dimensions of PTC5 being closest to the pre-set value (width of *ca.* 4 mm and thickness of *ca.* 2 mm) and the minimum dimension error. This could be due to the appropriate volume shrinkage of fuses, resulting from its moderate viscoelasticity (Figs. 3 and 4). However, the width and thickness of PTC9 are out of range of the preset values, resulting from the less shrinkage of fuses and in accordance with the previous viscoelasticity discussion.

Figs. 7(d)–7(h) show the SEM images of the fractured cross-section of PLLA and PTC tensile samples. Comparing Figs. 7(d) and 7(e), a failure that occurred across the layers (intra-layer and inter-layer) can be observed obviously in Figs. 7(f)–7(h), with PTC5 presenting the most obvious individual fuses failure by tension. Looking closely into the magnified zones of each sample (Figs. 7d₁–7h₁), typical sea-island structure can be observed except neat PLLA, with PTC5 presenting the finest phase morphology, which is consistent with the SEM results in Fig. 2 and the tensile properties above.

Effects of Infill Pattern and Infill Density on Mechanical Properties

It is well known that 3D printing parameters play an important

role in determining the properties of the final FDM parts.^[37,38] For instance, an investigation into the effects of different infill pattern and infill density on the impact and tensile strength of 3D printed PLLA parts have been reported, respectively.^[39,40] Based on the previous research mentioned above, we consider the influences of infill pattern and infill density on the PTC5 mechanical properties with the printing parameters in Table 1 under ambient temperature, including tensile and notch impact properties, as shown in Figs. S7 and S8 (in ESI). Only the conclusions are presented here:

(a) The FDM parts built with linear infill, such as Triangular, Rectilinear and Grid showed better tensile and impact properties, whereas parts built with curve infill, such as Honeycomb and Wiggle showed lower mechanical strength. This is because when printing with Honeycomb and Wiggle shapes, it will create a sudden change in direction and result in the jerk and vibration of extruder, leading to the uneven deposition and variation in material flow rate.^[40]

(b) The parts built with linear pattern (Rectilinear and Grid) infill at 100% density show the highest tensile strength, followed by 90%, 70% and 50% infill density. Because higher infill percentages improved the mechanical properties by providing more material to take the loads imposed by the tensile stress, consistent with the previous work.^[41] However,

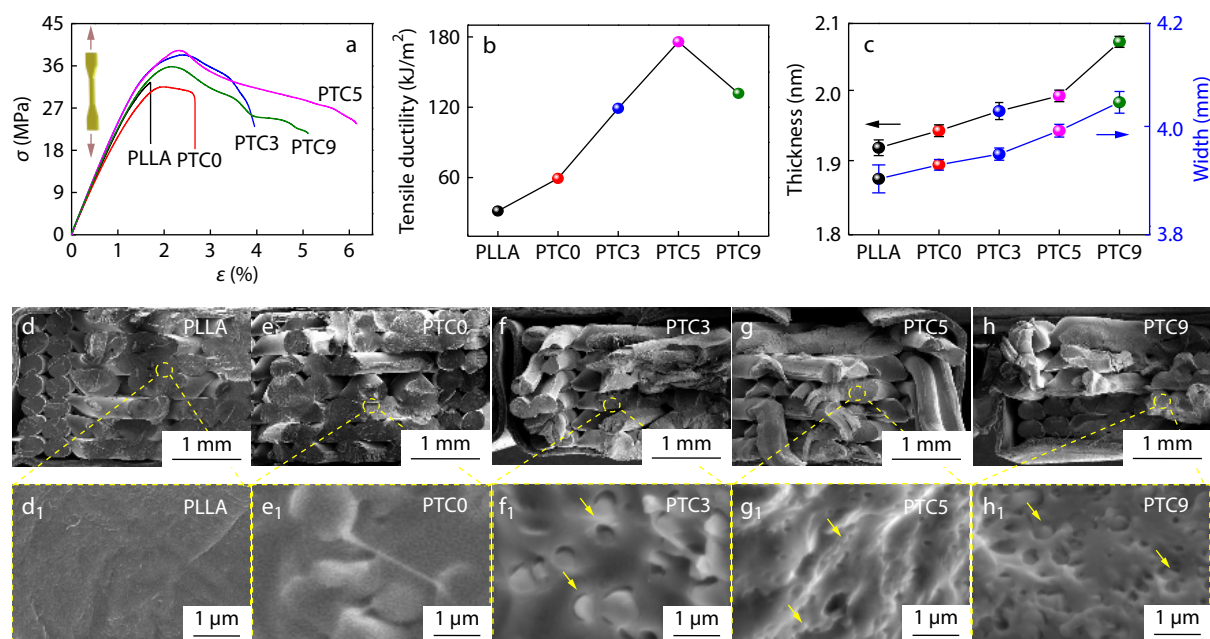


Fig. 7 (a) Stress-strain curves, (b) tensile ductility (the area under stress-strain curves), (c) dimensional stability, (d/d₁)–(h/h₁) SEM images of fracture surface of printed PLLA and PTC tensile parts.

the tensile strain has the opposite trend, due to the fact that as the percentage of infill density decreases, there is more air gap between fuses, and during the tensile loading some fuses filled this gap.

(c) The same conclusion of tensile strength above holds for the Notch impact with Rectilinear pattern at different infill density, where the impact strength at 100% infill density is highest followed by 90%, 70% and 50% infill density. However, due to the geometrical topology structure of the printed samples and their crack propagation under stress,^[39] the Notch impact with Grid pattern at 90% infill density was higher than that of samples with 100% infill density.

CONCLUSIONS

In this work, PLLA and PTC filaments with various CNCs-PVAc loadings were successfully prepared *via* simple melt processing for FDM. Both thermodynamic prediction, SEM and AFM micrographs demonstrated that CNCs nanoparticles were selectively and finely dispersed in PLLA, resulting from the good miscibility between PVAc and PLLA. This led to the increased melt elasticity of PLLA and decreased viscosity ratio of dispersed/matrix phases, therefore, facilitating the shear and immobilization of TPU droplets. In turn, this produced the refined PLLA/TPU phase morphology and diminished TPU droplets at nanoscale. Combined with the intensive shearing and continuous stretching forces during FDM, TPU droplets were connected with each other and deformed into *in situ* aligned fiber along the deposition direction. Both the refined TPU droplets and oriented TPU fiber structure made contributions to the superior mechanical properties, dimensional accuracy and surface performance of FDM parts. This work broadens the materials available for FDM and provides a new direction for stiffness and toughness balance of blends, which is meaningful to the final application of FDM

technology. Furthermore, the uniquely aligned TNFs would generate great potential for manufacturing materials with functions such as shape memory, electrical and thermal conductivity.

NOTES

The authors declare no competing financial interest.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at <http://doi.org/10.1007/s10118-022-2665-9>.

ACKNOWLEDGMENTS

The authors acknowledge the financial support from the National Natural Science Foundation of China (Nos. 21774068, 51503782) and Key Research and Development Program of Shaanxi Province of China (No. 2021GY-236).

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