

The Performance Investigation of PLLA/PPAPH: The Influence of PPAPH as Heterogeneous Crystal Nuclei

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Abstract: To overcome PLLA's poor crystallization capability, using nucleating agent as crystallization improvement strategy was performed in this study. PPAPH as PLLA's an organic nucleating agent was firstly synthesized, and then PLLA was blended with different PPAPH loading through melting blend method, the resulting influences of PPAPH on PLLA's performances were investigated using the relevant testing instruments. Melt-crystallization revealed that PPAPH played important role in promoting PLLA's crystallization through providing effective sites of heterogeneous nucleation, and effect of PPAPH loading on PLLA's melt-crystallization was very poor, indicating that low PPAPH loading could cause PLLA to possess powerful crystallization capacity. In addition, the relative low final melting temperature was beneficial for PLLA/PPAPH's crystallization. However, an increase of cooling rate during cooling stage weakened PLLA/PPAPH's crystallization capacity. PLLA/PPAPH's cold-crystallization suggested that PPAPH had an inhibition effect on cold-crystallization process to some extent. Melting behaviors depended on heating rate and previous crystallization including melt-crystallization at various cooling rates and isothermal crystallization at various crystallization temperatures. PPAPH enhanced PLLA's fluidity, tensile modulus and tensile strength. Unfortunately, PLLA's transmittance was seriously weakened as PPAPH loading increased, as well as the elongation at break continuously decreased.

Keywords: poly(L-lactide), phenylacetic hydrazide, heterogeneous nucleating agent, melt-crystallization, fluidity

1. Introduction

Introducing additives into polymer matrix is an important method for improving the performances of polymers or even developing new functionalities [1]. In terms of Poly(L-lactide) (PLLA), although PLLA presents some advantages such as high transparency [2], excellent degradability and biocompatibility [3, 4], high modulus [5], and easy processability [6], PLLA also suffers from several serious defects including slow crystallization rate, low crystallinity, poor heat resistance and low melt strength [7, 8], for this reason, the overall usage of PLLA by plastic manufacturers is hindered. Slow crystallization is regarded as one of the most serious defect in the present situation, because, on one hand, crystallization rate is directly related to the injection molding cycle which affects manufacturing cost of PLLA-based products; on the other hand, the resulting PLLA-based product's heat resistance and mechanical properties solely depend on crystallinity determined by the crystallization rate. For now, increasing the amount of L-lactide isomers and adding plasticizer or nucleating agent are thought to be three main ways of accelerating PLLA's crystallization process [9]. Whereas both increasing the amount of L-lactide isomers and adding plasticizer possess very remarkable disadvantages, for instance, the typical disadvantage of plasticizer in polymer resin is easy to overflow, resulting in a serious risk to environment and human health. In contrast, a nucleating agent possesses some typical advantages like extremely simple operation, low dosage and remarkable nucleation capability [10, 11], resulting in that a lot of researches focus on the influence of nucleating agents on PLLA's crystallization performance [12-19]. Inoue *et al* prepared a kind of inorganic/organic hybrid compound zinc phenylphosphonate to enhance PLLA's crystallization rate, the crystallization behaviors of PLLA modified by zinc phenyl-

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phosphonate showed that zinc phenylphosphonate had excellent acceleration effectiveness on PLLA's crystallization. When the crystallization temperature was 130°C, the crystallization half-times of PLLA nucleated by 15 wt% zinc phenylphosphonate decreased to only 0.33 min, and the epitaxial nucleation was proposed to be nucleation mechanism *via* structure analysis of zinc phenylphosphonate and PLLA [20].

Even then, a nucleating agent with higher acceleration capacity for PLLA's crystallization is still expected to meet more stringent requirements of industrial manufacturing. Through preliminary structural analysis of inorganic or organic nucleating agents, it is found that an organic nucleating agent exhibits a more flexible structural combination and favorable miscibility with PLLA matrix comparing with an inorganic nucleating agent [21], which is consistent with properties of efficient nucleating agent [22]. As a result, organic nucleating agents have been an important research hotspot in PLLA field, correspondingly, the organic nucleating agent has progressed to develop new compounds constructed through design and combination of molecular structure, and the final goal is to develop higher effectiveness organic heterogeneous nucleating agents. In this case, nucleation mechanism is crucial to develop effectiveness organic nucleating agents because of its theoretical basis role, whereas revealing nucleation mechanism must base on abundant organic molecules with different structures, and its purpose is to confirm that some specific organic groups and structures can enhance PLLA's crystallization capability. Unfortunately, this work is suffering from the limited categories and quantities of organic nucleating agents. Therefore developing any new organic nucleating agent is very meaningful to in-depth understand the structure-activity relationship of organic groups with nucleation capability.

Given that, *N, N'*-bis(phenylacetic) *p*-phthalic acid dihydrazide (PPAPH) was derived from phenylacetic hydrazide and *p*-phthalic acid, and this study was the first to use PPAPH as a new hetero-geneous additive to modify PLLA, and the influences of PPAPH on PLLA's melt-crystallization, cold-crystallization and melting processes were examined in detailed, additionally, PLLA/PPAPH's fluidity and optical property were also investigated by the related analytical instruments. This work could be of remarkable value to demonstrate the effect of some organic groups for PLLA's crystallization and reveal nucleation mechanism.

2. Materials and methods

Reagents and materials

The chemical reagents in this work include *N, N'*-dimethylformamide, *p*-phthalic acid, phenylacetic hydrazide, thionyl chloride and pyridine, and these analytically pure reagents were purchased from Chongqing Huanwei Chemical Company (China). In addition, these reagents were not further purified before usage. PLLA (trade name PLLA4032D) was produced by Nature Works (USA).

Preparation of PLLA/PPAPH

PPAPH needs to be synthesized in the lab before blending PLLA and PPAPH, and Figure 1 shows the synthetic route of PPAPH. It is clear that PPAPH's synthetic route includes two reaction stages, they are the acylation process of *p*-phthalic acid and amination process of phenylacetic hydrazide (The detailed operation process is similar to our previous works [17, 23]). The final white product PPAPH is further dried over night at 35°C under vacuum. Fourier Transform Infrared Spectrometer (FT-IR) ν : 3193.9, 3030.1, 1695.4, 1646.3, 1596.8, 1513.2, 1497.2, 1466.8, 1412.9, 1320.5, 1285.8, 1255.9, 1200.6, 1151.6, 1123.1, 1074.4, 1030, 893.7, 862.5, 695.1 cm^{-1} ; ^1H Nuclear Magnetic Resonance (^1H NMR) δ : ppm; 10.52 (s, 1H, NH), 10.25 (s, 1H, NH), 7.95~7.98 (d, 2H, Ar), 7.23~7.37 (m, 5H, Ar), 3.55 (s, 2H, CH₂).

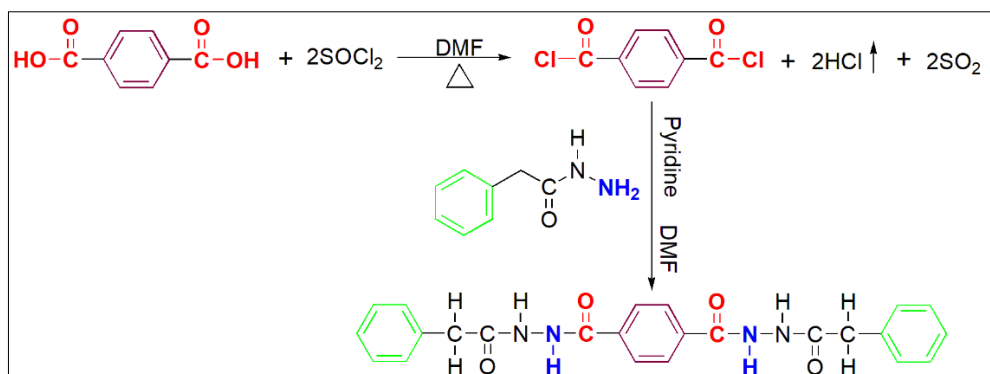


Figure 1. Synthetic route of PPAPH

The blending mass ratio of PLLA and PPAPH was firstly determined to be 100:0, 99.5:0.5, 99:1, 98:2 and 97:3, and the corresponding samples were designated as PLLA, PLLA/0.5%PPAPH, PLLA/1%PPAPH, PLLA/2%PPAPH and PLLA/3%PPAPH, respectively. The physical blending of PLLA and PPAPH was performed on a counter-rotating mixer, and physical blending parameters were set as follows: the blending temperature 190°C, the blending time 12 min (the rotation speed of 32 rpm for 7 min and rotation speed of 64 rpm for 5 min). The resulting mixture was further processed using flat-panel curing machine to prepare PLLA and four PLLA/PPAPH samples with a thickness of 0.4 mm, the specific process included hot-pressing by 20 MPa at 180°C and cool-pressing at room temperature.

Characterization and test

For PPAPH's structure characterization, PPAPH molecular structure was characterized by Nicolet iS50 FT-IR (Thermo Scientific, USA) and 400 MHz ^1H NMR (Bruker, USA), the testing wavenumber of FT-IR characterization was from 4000 cm^{-1} to 400 cm^{-1} , and KBr pellet was employed to prepare FT-IR testing sample of PPAPH; a trace of PPAPH was dissolved by dimethyl sulfoxide as deuterium reagent to perform ^1H NMR characterization. PLLA/PPAPH's crystallization and melting process tests were recorded by Q2000 DSC (TA instrument, USA) with 50 mL/min nitrogen, the temperature and heat flow was calibrated using an indium standard, and then all testing samples needed to be heated to the melt to eliminate thermal history, final the related tests were carried out and recorded according to different testing procedures. For the fluidity test of PLLA and PLLA/PPAPH, the fluidity was determined by the melt index instrument, and the testing temperature was 180°C. For optical property test, DR82 transmittance instrument was used to test the transmittance of PLLA and PLLA/PPAPH, and the final transmittance was determined through calculating the average of five times measurements. The mechanical properties of PLLA and PLLA/PPAPH were performed on a D&G DX-10000 electronic tensile tester (1 mm/min stretching speed) at room temperature for three tests, and the elongation at break, tensile modulus and tensile strength were obtained *via* calculating average value.

3. Results and discussions

Melt-crystallization process

Usually, the discernible method for estimating nucleation role of an additive is investigating on melt-crystallization process of polymer modified by an additive. Figure 2 displays DSC thermograms of pure PLLA and PLLA with various PPAPH loadings from 190°C at the cooling rate of 1°C/min. As seen in Figure 2, all PLLA/PPAPH samples have obvious and sharp melt-crystallization peaks, whereas pure PLLA does almost not have observable melt-crystallization peak upon cooling at 1°C/min. This finding shows that, on one hand, pure PLLA cannot form crystal in cooling because of its rather poor crystallization capability; on the other hand, PPAPH plays the role of a heterogeneous nucleating agent in cooling to improve PLLA's crystallization. Additionally, the influences of PPAPH loading on PLLA's melt-crystallization behavior are concluded into three types. When PPAPH loading is from 0.5 wt% to 1 wt%, the melt-crystallization peak slightly shifts toward high-temperature side. When increasing

PPAPH loading from 1 wt% to 2 wt%, the melt-crystallization peak exhibits a tiny shift to low-temperature level. Further increasing PPAPH loading to 3 wt%, the melt-crystallization peak moves toward high-temperature side again, but the range of change is very tiny. Overall, the influence of PPAPH loading on PLLA's melt-crystallization is very poor through data analysis of onset crystallization temperature (T_{oc}), crystallization peak temperature (T_{mc}) and melt-crystallization enthalpy (ΔH_c), illustrating that a small amount of PPAPH possesses excellent crystallization promoting capability for PLLA's crystallization. Among all PLLA/PPAPH, PLLA/1%PPAPH exhibits the highest T_{oc} at 138.8°C and the highest T_{mc} at 135.7°C, as well as the largest ΔH_c of 52.5 J/g which means that PLLA/1%PPAPH's crystallinity is up to 57.0% through calculation [24]. These results also show that, upon the addition of 1 wt% nucleating agent, the T_{oc} , T_{mc} and ΔH_c of PLLA/PPAPH are higher than PLLA/BHADD [25].

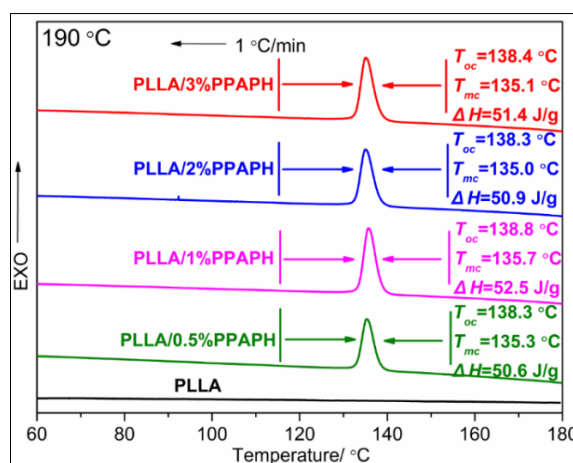


Figure 2. Melt-crystallization of pure PLLA and PLLA/PPAPH from the melt of 190°C at a cooling rate of 1°C/min

PPAPH's crystallization accelerating role has been confirmed in previous melt-crystallization section upon cooling at 1°C/min, but the cooling rate is very slow, which is insufficient to demonstrate PPAPH powerful role in accelerating PLLA's crystallization rate, because the actual manufacturing process often requires a higher cooling rate. Therefore the effects of various cooling rates (10°C/min, 20°C/min and 40°C/min) on PLLA's melt-crystallization behavior were further studied as shown in Figure 3. For any PLLA/PPAPH sample, it is observed that, with an increase of cooling rate from 10°C/min to 40°C/min, there exists still obvious melt-crystallization peak, which confirms powerful nucleation capability of PPAPH for PLLA's crystallization again. However, a faster cooling rate makes melt-crystallization peak shift to low-temperature side, and the intensity of peak also gradually reduce, indicating that PLLA/PPAPH's nucleation capability has been controlled by thermal dynamics [26]. This result is thought to may be the fact that rearrangement of PLLA chains into the lattice takes some time and the cooling is too fast to lag the crystallization process [27]. In addition, it should be noted that a higher PPAPH loading has a greater inhibition for the decrease of PLLA's crystallization capability with continuously increase in cooling rate, especially when the cooling rate is 40°C/min, the melt-crystallization peak of PLLA containing a higher PPAPH loading locates in the higher temperature side, showing a more powerful crystallization capability.

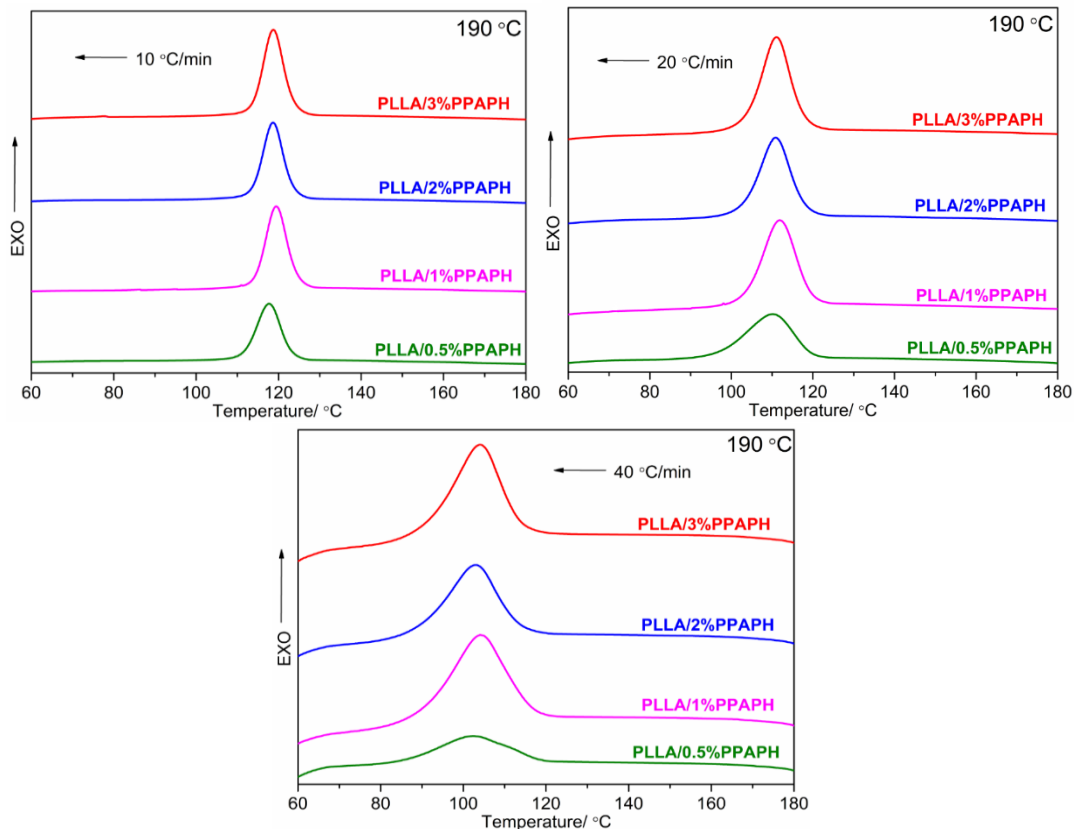
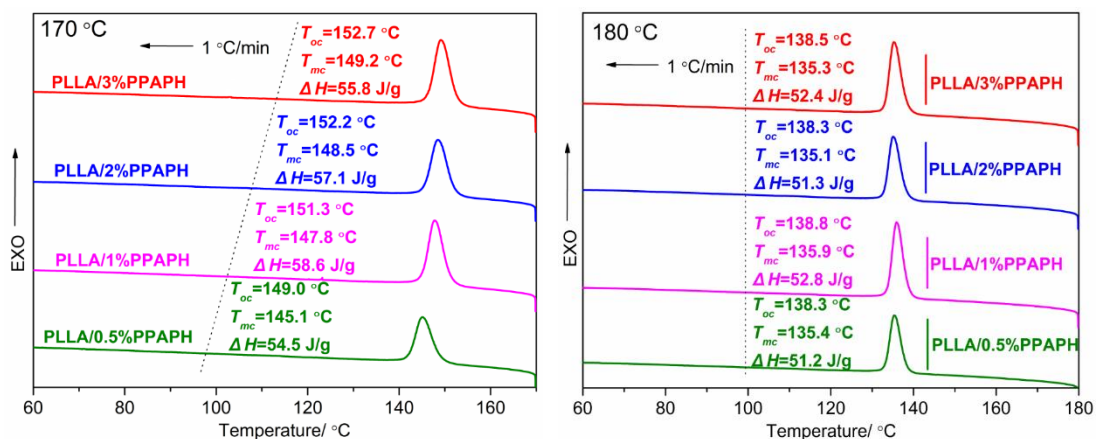


Figure 3. Melt-crystallization of PLLA/PPAPH from the melt of 190°C at various cooling rates

For extrusion injection molding, the optimal processing temperature range is very important index to regulate the dispersion of additive and control the resulting performances. Figure 4 shows that the effect of the final melting temperature (T_f) on PLLA's melt-crystallization behavior. It is clearly seen that, in comparison to other T_f , there exists the highest T_{oc} , T_{mc} and the largest ΔH_c when the T_f is 170°C, implying that a relative low T_f is beneficial for PLLA/PPAPH's crystallization, the probable reason is that a relative low T_f cannot dissolve more PPAPH in PLLA, resulting in that the undissolved PPAPH particles become nuclei for PLLA's crystallization in cooling and the dissolved PPAPH, as well as form higher nucleation density in PLLA which induces occurrence of crystallization at higher temperature. More specifically, the melt-crystallization peak of any PLLA/PPAPH shifts toward low-temperature side with increasing of T_f from 170°C to 190°C, afterwards, the melt-crystallization parameters moderately increase when T_f is increased to 200°C. Additionally, when the T_f is 170°C, the melt-crystallization appears at higher-temperature location as PPAPH loading increased, whereas the effect of PPAPH loading on PLLA's melt-crystallization is very weak as seen in Figure 5, when the T_f is not 170°C.



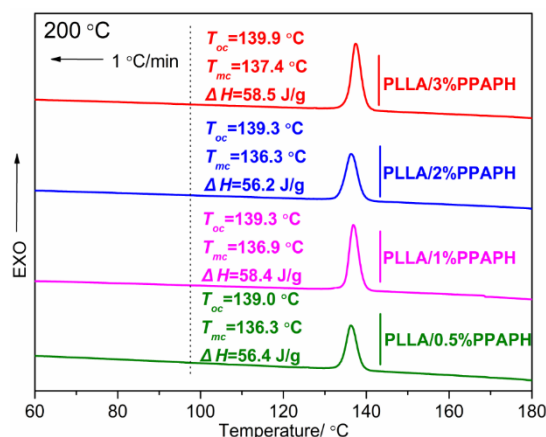
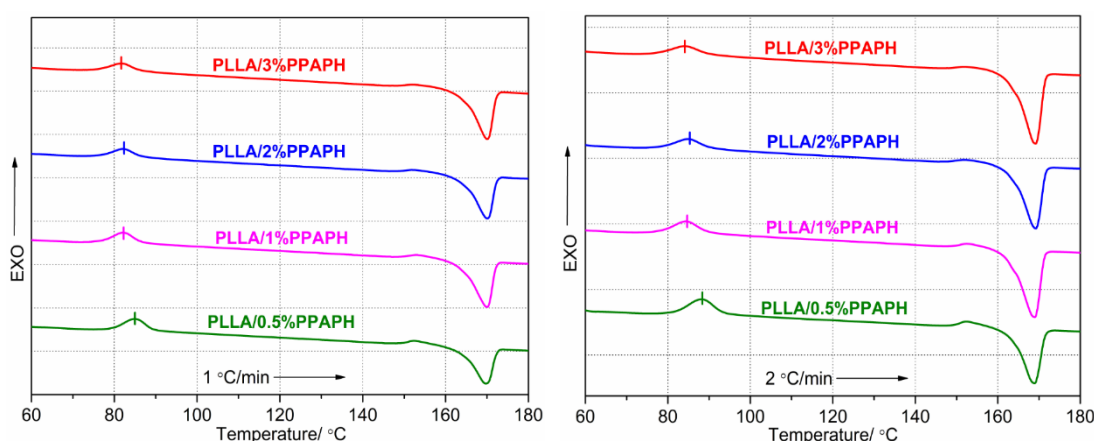


Figure 4. Melt-crystallization of PLLA/PPAPH from different T_f at a cooling rate of 1°C/min

Cold-crystallization process

As reported [28, 29], the crystallization process in heating is different from melt-crystallization process in cooling due to different nucleation rate and crystal growth rate. Figure. 5 shows cold-crystallization processes of PLLA/PPAPH in heating at various rates (1°C/min, 2°C/min and 5°C/min). Figure 5 exhibits two distinct features, one feature is that, with increasing of PPAPH loading, the cold-crystallization peak moves toward low-temperature side and peak's intensity also becomes weak, indicating that PPAPH has an inhibition for PLLA's cold-crystallization process to some extent, which is consistent with effects of other additives on cold-crystallization process [17, 30]; another feature is that, with an increase of heating rate, cold-crystallization peak of a given PLLA/PPAPH shifts toward high-temperature side, which originates from the thermal inertia. However, upon a definite heating rate, a larger amount of PPAPH can cause melting peak to locate in higher temperature side, whereas a faster heating rate leads to a moderate shift of melting peak to low-temperature side, the probable reason is that a faster heating rate makes PLLA macromolecule segment not rapidly form a regular structure and crystals cannot be grown better, resulting in formation of imperfect crystals, and these imperfect crystals are firstly melted during heating procedure.



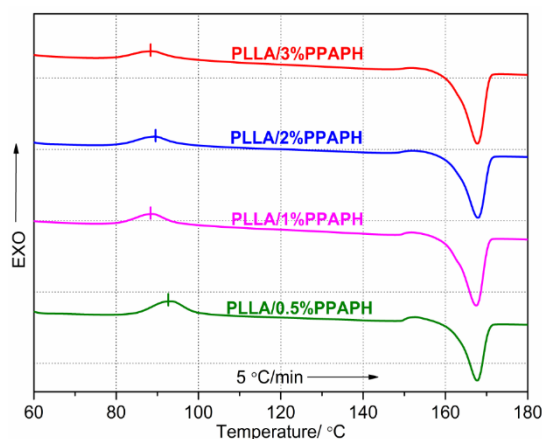


Figure 5. Cold-crystallization of PLLA/PPAPH at various heating rates

Melting behavior

PLLA/PPAPH's melting processes after non-isothermal melt-crystallization and isothermal crystallization are further investigated by DSC. Figure 6 is PLLA/PPAPH's melting behaviors at different heating rates that corresponded to the rates of non-isothermal melt-crystallization at different cooling rates. It can be clearly observed that all PLLA/PPAPH have discernible double melting peaks at heating rates of 2°C/min and 5°C/min, in terms of PLLA's double melting peaks, the melting-recrystallization mechanism is used to explain this phenomenon of double melting peaks [31, 32], the high-temperature melting peak is attributed to the melt of crystallites reformed during the heating, and the low-temperature melting peak results from the melt of the primary crystallites formed in cooling. However, when the heating rate is 1°C/min, PLLA/PPAPH exhibits very weak high-temperature melting peak, meaning that most of crystallization has been completed in cooling stage and few crystals are formed in following heating stage, this result further evidences remarkable influence of cooling rate on PLLA's crystallization to some extent.

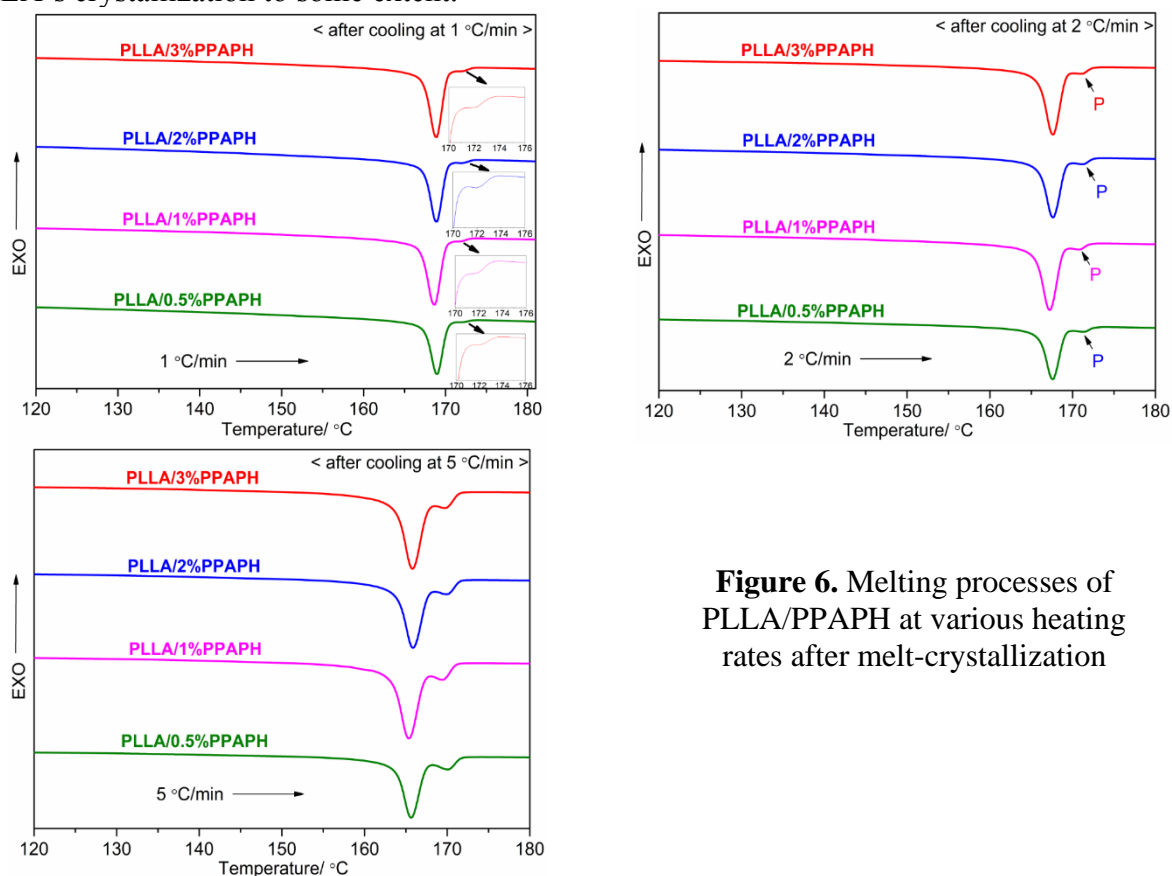
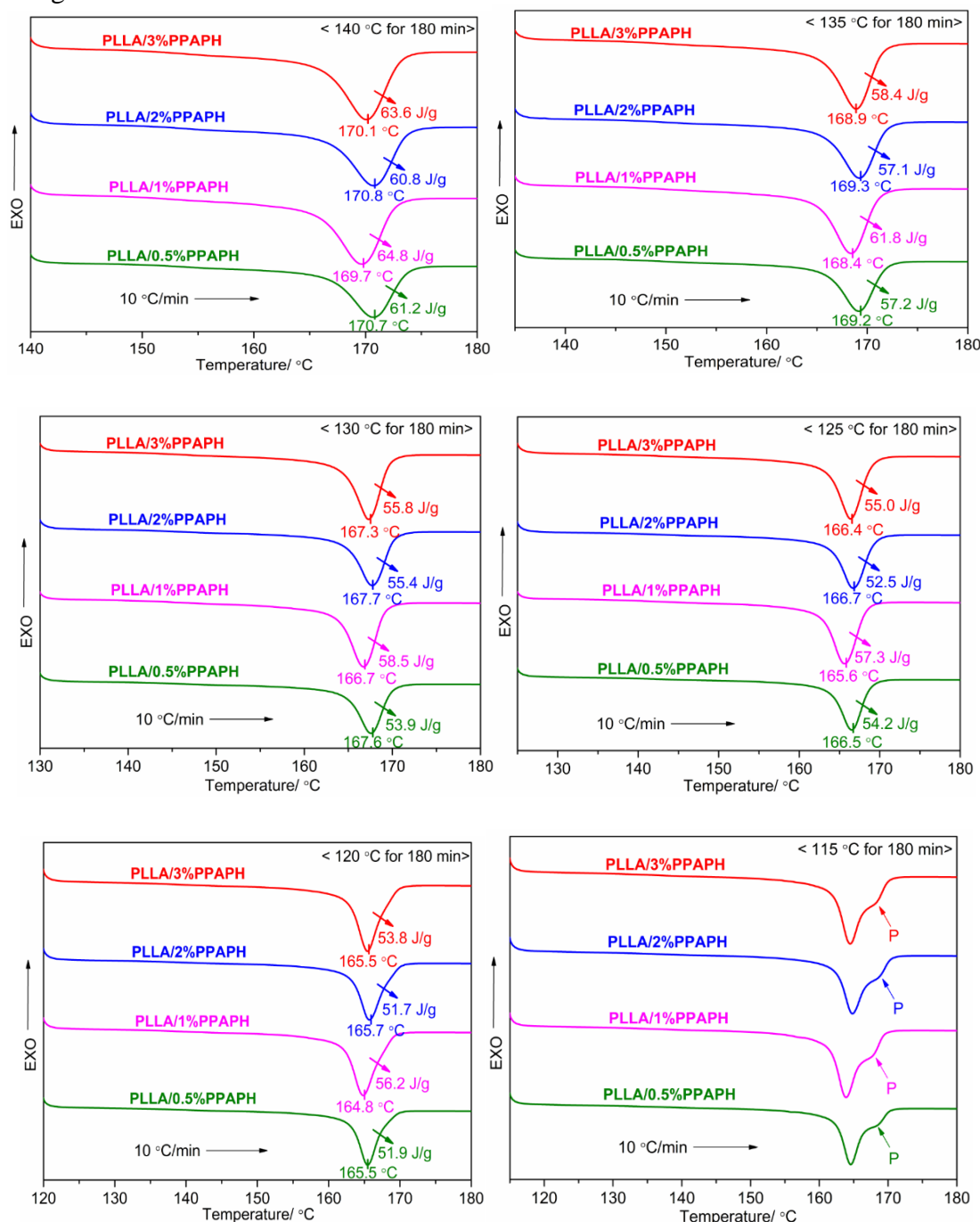


Figure 6. Melting processes of PLLA/PPAPH at various heating rates after melt-crystallization

Figure 7 presents PLLA/PPAPH's melting behaviors after isothermal crystallization at different crystallization temperatures for sufficient time. As seen in Figure 7, with decreasing of crystallization temperature from 140°C to 110°C, the single melting peak gradually changes to double melting peaks, showing that a relative low crystallization temperature is not favorable to sufficient crystallization, because the migration of PLLA molecular segment is very poor in low-temperature region, leading to a very slow crystal growth rate and insufficient crystallization, as well as imperfect crystal. Additionally, the melting peak temperature and melting enthalpy also shows a downward trend with decreasing of crystallization temperature, which is also related to crystallization. That is, long enough crystallization time can ensure that the crystallization is completed in high-temperature region and the formed crystals are also very perfect due to the nucleation effect of PPAPH and excellent migration ability of PLLA molecular segment.



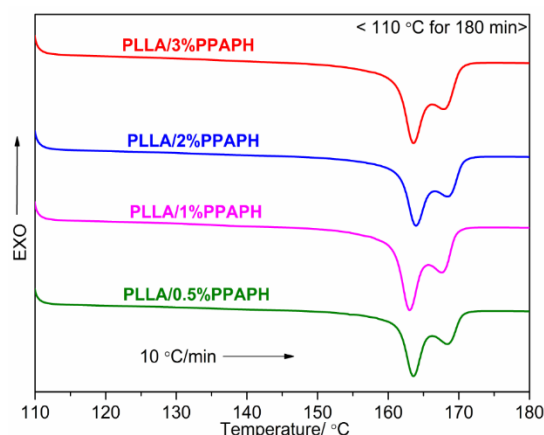


Figure 7. Melting processes of PLLA/PPAPH at a heating rate of 10°C/min after isothermal crystallization at different temperatures

Fluidity and optical property

The fluidity of pure PLLA and PLLA/PPAPH is determined through testing melt flow rate (MFR) of the corresponding sample. Figure 8 is MFR of pure PLLA and PLLA/PPAPH. It is observed that MFR increases from 1.67 g/10min to the maximum value of 9.81 g/10min with an increase in PPAPH loading from 0 wt% to 1 wt%. After that, with the addition of 2 wt% PPAPH, MFR decreases to 5.8 g/10min. Whereas MFR exhibits a very tiny change when further increasing PPAPH loading, indicating that the effect of PPAPH loading on MFR is negligible in this study when PPAPH loading is 2 wt% ~ 3 wt%. However, MFR of any PLLA/PPAPH is higher than pure PLLA, suggesting that the addition of PPAPH enhances PLLA’s fluidity, the reason may be that the interaction between C=O of PLLA molecular chain and N-H of PPAPH can be formed more easily during melting blend than PLLA molecular chain itself *via* frontier orbital energy calculation as shown in Figure 9, because the HOMO and LUMO of PLLA containing ten units are -11.082 eV and 0.251 eV, the HOMO and LUMO are -0.211 eV and -0.115 eV for PPAPH, as a result, the LUMO-HOMO energy gap between LUMO of PPAPH and HOMO of PLLA is smaller than that PLLA itself, indicating that PLLA’s electrons flow more easily to PLLA’s LUMO in the melting blend stage, which results in that the interaction of PLLA molecular chains is destroyed more strongly, promoting PLLA’s fluidity to enhance.

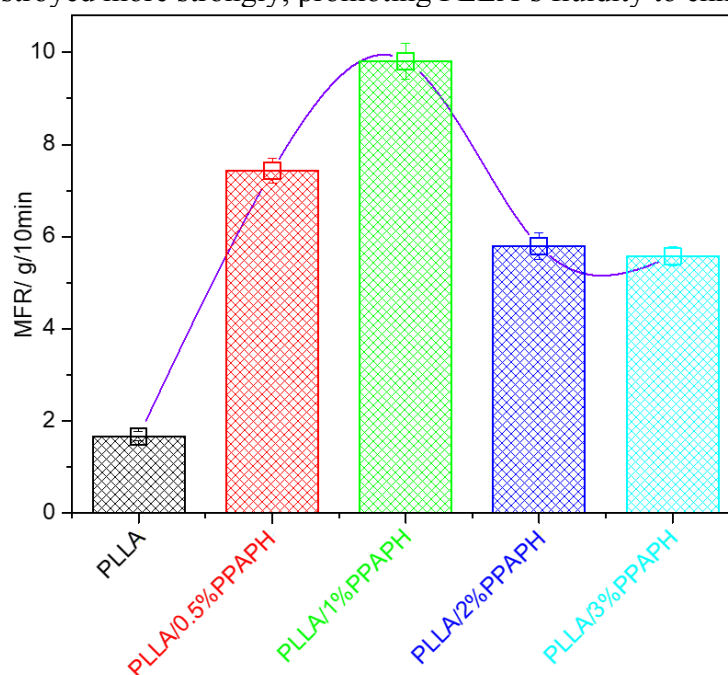


Figure 8. MFR of pure PLLA and PLLA/PPAPH

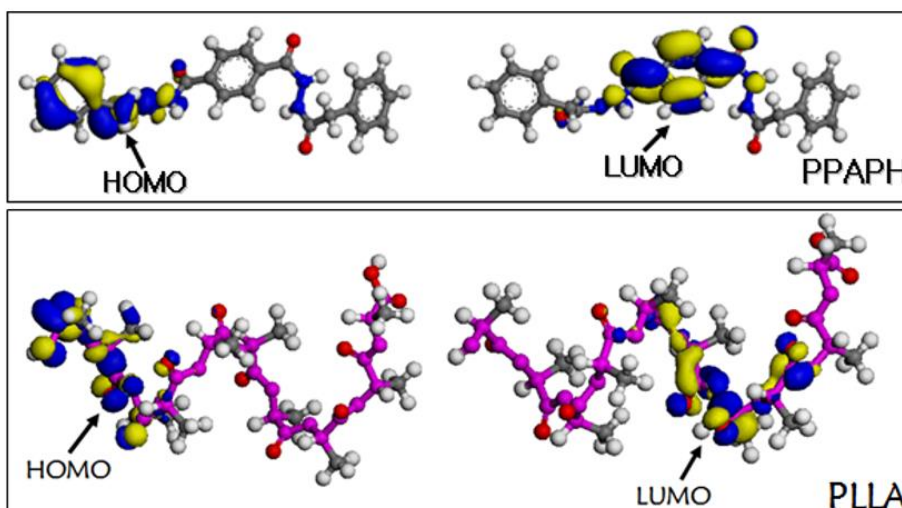


Figure 9. Frontier orbital of PLLA and PPAPH

The introduction of a nucleating agent often destroys PLLA's transmittance, which is attributed to two reasons, one reason is that the high crystallinity can increase PLLA's haze, because the higher the crystallinity is, the higher the haze is; another reason is that the color of a nucleating agent itself can also decrease PLLA's transmittance. These effects are confirmed again as seen in Figure 10. The addition of PPAPH significantly increases PLLA's haze, and upon the addition of 0.5 wt% PPAPH, the transmittance decreases from 78.2% to 9.77%, exhibiting a high haze and low transmittance. Further increasing PPAPH loading, the haze increases, when PPAPH loading is 2 wt%, the transmittance is almost zero.

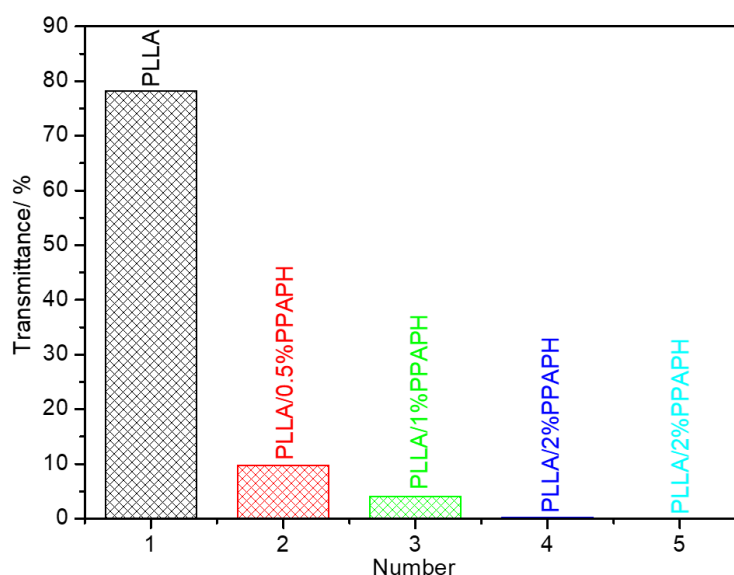


Figure 10. Transmittance of pure PLLA and PLLA/PPAPH

Mechanical properties

The mechanical properties of pure PLLA and PLLA containing various PPAPH loading were listed in Table 1. In terms of the elongation at break, the introduction of PPAPH reduces PLLA's plasticity, because the elongation at break continuously decreases from 6.9% to 3.6% with increasing of PPAPH loading from 0 wt% to 3 wt%, the reason is that, on one hand, the addition of PPAPH increases PLLA's brittleness due to the brittleness of PPAPH itself; on the other hand, PPAPH promotes PLLA's crystallization, and an increase of crystallinity must lead to a greater brittleness. In terms of the tensile modulus and tensile strength, both the tensile modulus and tensile strength cannot show the continuous



changes with increasing of PPAPH loading, but the tensile modulus and tensile strength of any PLLA/PPAPH are higher than these of pure PLLA, showing that PPAPH enhances PLLA's tensile modulus and tensile strength.

Table 1. Mechanical properties of pure PLLA and PLLA containing different PPAPH loading

Sample	Elongation at break / %	Tensile modulus / MPa	Tensile strength / MPa
PLLA	6.9	1536.6	41.7
PLLA/0.5% PPAPH	4.2	1947.6	47.3
PLLA/1% PPAPH	4.0	1841.4	43.2
PLLA/2% PPAPH	3.7	1873.7	49.2
PLLA/3% PPAPH	3.6	1891.4	46.3

4. Conclusions

In this study, PPAPH was blended with PLLA to estimate its influence on PLLA's performance, melt-crystallization test illustrated that PPAPH could significantly boosted PLLA's crystallization performance through inducing PLLA crystallization at higher temperature and accelerating PLLA's crystallization rate. Upon cooling at 1°C/min, PLLA/1%PPAPH possessed the best crystallization performance, but generally the influence of PPAPH loading on PLLA non-isothermal melt-crystallization was very poor. The investigation on effects of cooling rate and T_f on melt-crystallization showed that a faster cooling rate weakened PLLA/PPAPH's crystallization capability, and that PLLA/PPAPH exhibited better crystallization performance when cooling from the melt of 170°C. Cold-crystallization testing results showed that a larger amount of PPAPH promoted crystallization peak to appear in lower temperature region, indicating that PPAPH had an inhibition effect on cold-crystallization process. For PLLA/PPAPH's melting behaviors, both previous crystallization and heating rate in heating exhibited significant influence on following melting processes, and the appearance of double melting peaks was thought to be due to melting-recrystallization. Compared to pure PLLA, PLLA/PPAPH had better fluidity, and this effect depended on the destructive role of PPAPH for interactions of PLLA molecular chains, which was confirmed by frontier orbital energy calculation results. The optical property showed that the presence of PPAPH was very detrimental to PLLA's transmittance, and the results from mechanical property further showed that PPAPH reduced PLLA's plasticity because of a decrease in the elongation at break, but the addition of PPAPH could enhance the tensile modulus and tensile strength.

Acknowledgements: This work was supported by Chongqing Science and Technology Bureau (CSTB2023NSCQ-MSX1087), Chongqing Municipal Education Commission (KJZD-K202301303) and Chongqing University of Arts and Sciences (project number P2020HH06 and Y2022HH02).

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Manuscript received: 04.05.2023