

Non-isothermal melt- and cold-crystallization, melting process, and optical and mechanical properties of PLLA: the effect of TAPH

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We synthesized a new phenylacetic hydrazide derivative (TAPH) by acylation and amination to prepare modified poly(L-lactide) (PLLA) materials. The non-isothermal melt- and cold-crystallization, melting process, optical and mechanical properties of modified PLLA were studied with the objective of correlating TAPH to PLLA crystallization and other performances. Non-isothermal melt crystallization showed that TAPH as a heterogeneous additive was able to promote crystallization and accelerate the crystallization rate of PLLA. Unfortunately, an increase in the cooling rate during cooling led to a decrease in crystallization ability. Non-isothermal cold-crystallization results disclosed that PLLA/TAPH's cold-crystallization behavior depended on the heating rate; and upon a given heating rate, with an increase in TAPH loading, a shift toward the low-temperature side of the cold-crystallization peak further confirmed the nucleation effect of TAPH. The melting processes of PLLA/TAPH effectively depended on TAPH, the heating rate, and previous crystallization behaviors including non-isothermal crystallization and isothermal crystallization. Additionally, the double-melting peaks that appeared during the melt were thought to be due to melting-recrystallization. In terms of the optical property, the influence of TAPH on PLLA's transparency was extremely negative as 2 wt% TAPH caused PLLA's transparency to be zero. A comparative study on mechanical properties showed that TAPH could enhance PLLA's tensile modulus and tensile strength, but elongation at break of any PLLA/TAPH was lower than that of pure PLLA.

Keywords: *poly(L-lactide)*, *phenylacetic hydrazide*, *non-isothermal crystallization*, *thermal behaviors*, *mechanical properties*

1. Introduction

Currently, degradable plastics have become more and more popular on a global scale due to the serious environmental pollution that has originated from large-scale usage of petroleum-based and non-degradable plastics. Poly(L-lactide) (PLLA) is one of the most promising degradable thermoplastic polyesters, and its features, including excellent biocompatibility and biodegradability [1], good transparency [2], excellent mechanical properties [3], and good thermoplastic processability [4], explain its increasing applications in a large range of fields. For example, Lv *et al* [5] investigated the hemostatic effects of Fe³⁺-modified biomimetic PLLA cotton-like mat. First, the cotton-like biomimetic fibrous mat of PLLA and sodium alginate/dopamine composite were

prepared *via* melt spinning and cross-linking technology, respectively and Fe³⁺ was loaded onto the PLLA composite containing the sodium alginate/dopamine composite. The related experiment results showed that Fe³⁺-modified biomimetic PLLA cotton-like mat *via* sodium alginate grafted with dopamine could have a dramatically improved hemostatic property. Additionally, it also exhibited an excellent anti-bacterial property for *Escherichia coli* and *Staphylococcus aureus*.

Notwithstanding, the application of PLLA suffers from some impediments that result from PLLA's intrinsic defects such as slow crystallization rate, low thermal deformation temperature, slow degradation rate, and low melt strength [6, 7]. Thus, enhancing PLLA's related performance is necessary to fully compete with commercial thermoplastic materials such as polypropylene, polyethylene, and polycarbonate. According to the

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current industrial manufacturing requirements for the efficiency and high performance of PLLA products, solving the problem of slow crystallization rate is crucial because the molding cycle during manufacturing and the resulting product's heat resistance depend on PLLA's crystallization rate. Currently, the utilization of a nucleating agent is regarded as one of the most effective and easiest ways to accelerate PLLA's crystallization rate [7]. In terms of accelerating crystallization rate *via* a nucleating agent, nucleating agent as an additive can provide a heterogeneous nucleation site and increase nucleation density in the polymer matrix, as well as decrease the nucleation barrier to induce the occurrence of crystallization in a higher temperature region or at a faster cooling rate. Up to now, a larger number of chemical substances have been employed to estimate their possibilities as a nucleating agent for PLLA's crystallization, and a considerable number of compounds have exhibited a powerful role in promoting PLLA's crystallization ability. These compounds can be divided into three categories according to molecular structure: inorganic nucleating agents, organic nucleating agents, and inorganic/organic hybrid nucleating agents. The typical inorganic nucleating agents include CaCO_3 [8], zinc citrate [9, 10], talc [11, 12], and WS_2 [13]; TMC series [14–16], benzotriazole derivatives [17, 18], fulvic acid derivatives [19, 20], and sorbitol and its derivatives [21–23]. Piperonylic acid derivatives [24, 25] are typical organic nucleating agents, and metal phosphonates [26, 27], salts of phenylmalonic acid [28, 29], and metal-organic frameworks [30] are the main inorganic/organic hybrid nucleating agents. Unfortunately, inorganic nucleating agents are thought to be difficult to disperse into PLLA uniformly and have poor compatibility with PLLA [31], which can seriously affect the performance of PLLA products. In contrast, organic nucleating agents have better compatibility with PLLA and tend to disperse well in the PLLA matrix while significantly accelerating PLLA's crystallization rate [31, 32]. Thus, developing more new organic nucleating agents has become an active topic of research about PLLA crystallization, and a certain amount of synthetic organic compounds

have been used to serve as heterogeneous nucleating agents for PLLA crystallization [33, 34]. Nevertheless, a more efficient organic nucleating agent is still continuously expected by industrial manufacturing. Moreover, compared to an inorganic nucleating agent, the nucleation mechanism of organic nucleating agents for PLLA crystallization is more complicated because there are more influencing factors such as functional groups, intermolecular interaction, and space structure. Thus, scientific research and industrial manufacturing urgently need to develop more new organic nucleating agents to further confirm the structure-activity relationships, including amide groups and their nucleation role, ring structure and its nucleation role, and molecular electron density and its nucleation role. For the aforementioned purpose, in this work, an organic compound with multiple benzenes and amide groups (designated as TAPH) as a crystallization performance improvement strategy was synthesized to try to manipulate PLLA's crystallization, and melt crystallization, cold crystallization, melting processes after crystallization, optical performance, and mechanical properties of TAPH-nucleated PLLA were studied in depth *via* various testing instruments including differential scanning calorimeter (DSC), transmittance instrument, and electronic tensile tester. This study may be helpful in providing a development strategy for organic nucleators and explores the role of key organic structures, as well as promoting the commercialization of nucleators for PLLA.

2. Experimental section

2.1. Chemical reagents and materials

TAPH was obtained in our lab through two-step liquid reactions, namely, acylation and amination, and all analytical purity reagents were directly used without further purification. These chemical reagents were 1, 3, 5-benzenetricarboxylic acid, thionyl chloride, phenylacetic hydrazide, *N,N*-dimethylformamide (DMF), and pyridine. PLLA in this work was a commercial-grade product (trade name 4032D PLLA) that was produced by Nature-Works Company.

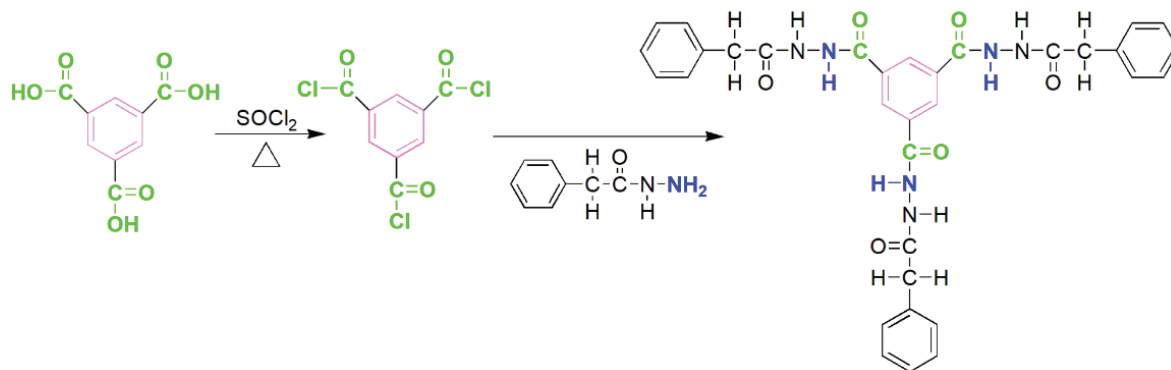


Fig. 1. Synthetic route of TAPH

2.2. Synthesis of TAPH and preparation of PLLA/TAPH

Synthesis of TAPH was performed according to the designed synthetic route as shown in Figure 1. First, to obtain enough trimesoyl chloride, 0.035 mol of 1, 3, 5-benzenetricarboxylic acid, 70 mL of thionyl chloride, and 2.5 mL of DMF were mixed in a three-necked flask of 250 mL, and the mixture was slowly heated up to 80°C with stirring to reflux for 36 h. After this, the cooled solution was vacuum distilled to obtain pale yellow trimesoyl chloride. Second, 0.003 mol of phenylacetic hydrazide was dissolved into a liquid mixture containing 70 mL of DMF and 2 mL of pyridine, and then 0.001 mol of trimesoyl chloride was added into the aforementioned liquid mixture with stirring. The mixture was stirred at room temperature for 1.5 h, and then the mixture was heated up to 70°C for further reaction for 2 h with stirring. The reaction mixture was poured onto 300 mL of water to deposit overnight, and the deposition was filtrated to obtain the crude product, followed by washing three times to obtain the resulting white TAPH. Finally, TAPH was dried overnight at 40°C under vacuum. FT-IR (KBr) ν : 3586.1, 3246.2, 3030.6, 1695.5, 1656.7, 1610, 1584, 1496.1, 1454.3, 1432.3, 1300.5, 1246.4, 1197.4, 1137.3, 1074.9, 1030.7, 982.6, 913, 776.9, 723.3, and 695.1 cm^{-1} ; ^1H NMR (Deuterated dimethyl sulfoxide, 400 Hz) δ : ppm; 10.67 (s, 1H, NH), 10.34 (s, 1H, NH), 7.96~7.99 (d, 1H, Ar, $J=12$ Hz), 7.23~7.37 (m, 5H, Ar), and 3.55~3.56 (d, 2H, CH_2 , $J=4$ Hz).

In this work, we employed melting blend technology to fabricate PLLA/TAPH and the detailed blending operation was as follows: PLLA and TAPH were first mixed according to the set mass ratio (100:0, 99.5:0.5, 99:1, 98:2 and 97:3, the resulting modified samples were labeled as PLLA, PLLA/0.5%TAPH, PLLA/1%TAPH, PLLA/2%TAPH, and PLLA/3%TAPH, respectively), and then the mixture was poured into a counter-rotating mixer to perform the blending operation, which included two stages. For the first stage, there was a blending temperature of 190°C, a blending time of 7 min, and a rotation rate of 32 rpm. For the second stage, there was a blending temperature of 190°C, a blending time of 5 min, and a rotation rate of 64 rpm. After this, the mixture was further hot pressed at 190°C and cool pressed at room temperature under 20 MPa to obtain films with a thickness of 0.4 mm, and all samples for the tests were cut from these films.

2.3. Characterization and test

TAPH's molecular structure was determined through FT-IR and ^1H NMR characterization, and the testing conditions for FT-IR and ^1H NMR characterization were as follows: KBr pellet method for sample preparation and wavenumber from 4000 cm^{-1} to 400 cm^{-1} for the FT-IR test and deuterated dimethyl sulfoxide as solvent for the ^1H NMR test. For non-isothermal melt crystallization and the subsequent melting process recorded by Q2000 DSC, pure PLLA and PLLA/TAPH were

heated to 190°C for holding for 3 min to eliminate thermal history, and then cooled at different cooling rates (1°C/min, 2.5°C/min, 5°C/min, 10°C/min, and 20°C/min) to 40°C, and heated again to 190°C at a heating rate of 10°C/min. Additionally, the heating rates after melt crystallization upon cooling at 1°C/min were 1°C/min, 2°C/min, 4°C/min, 8°C/min, and 16°C/min. For the cool-crystallization process, PLLA/TAPH was heated to 190°C and jumped to 40°C for holding for 3 min, and heated to 180°C again at different heating rates (1°C/min, 2.5°C/min, and 5°C/min), and the corresponding process data were recorded by DSC. For the melting behavior after isothermal crystallization, PLLA/TAPH was heated to 190°C and jumped to set crystallization temperatures (110°C, 115°C, 120°C, 125°C, 130°C, and 135°C) for isothermal crystallization for 180 min, and then PLLA/TAPH was heated to 190°C at a heating rate of 10°C/min, and the heating process was also recorded by DSC. The effect of TAPH on the light transmittance of PLLA was tested by a DR82 transmittance instrument, and the light transmittance of a given PLLA/TAPH was obtained by calculating the average value of five measurements. The tests for mechanical properties were conducted on a D&G DX-10000 electronic tensile tester, and the stretching speed was set to be 5 mm/min, and the dimensions of the testing sample was 25 mm×4 mm×0.5 mm.

3. Results and discussion

3.1. Non-isothermal melt crystallization

Estimating non-isothermal melt crystallization behavior is very important as this corresponds to actual industrial applications. Figure 2 shows the DSC cooling curves of pure PLLA and PLLA/TAPH from the melt of 190°C at a rate of 1°C/min. As expected, pure PLLA almost did not present a crystallization peak on the DSC cooling curve because of the poor nucleation ability and slow movement of the PLLA chains [35]. In contrast, when TAPH is introduced into PLLA, TAPH influences PLLA's crystallization, and very obvious non-isothermal melt-crystallization peaks

are observed on the DSC cooling curves of all PLLA/TAPH, indicating that TAPH acts as a heterogeneous nucleating agent in the PLLA matrix and effectively enhances PLLA's crystallization. Because the existence of TAPH increases PLLA's nucleation density, as a result, the nucleation rate of PLLA/TAPH becomes fast. In addition, the cooling rate of 1°C/min can ensure that the PLLA segment has time to form a regular structure for promoting crystal growth. Ultimately, the synergistic effect of a fast nucleation rate and crystal growth rate leads to the appearance of a non-isothermal melt-crystallization peak on the DSC cooling curve. The influence of TAPH's concentration on the non-isothermal melt-crystallization behavior of PLLA is displayed in Figure 2, and it can be clearly observed that TAPH's concentration has less effect on PLLA's non-isothermal melt crystallization, and the maximum differences of non-isothermal melt-crystallization peak temperature and melt-crystallization enthalpy are only 2.1°C and 1.6 J/g, respectively. Furthermore, when TAPH concentration is 0.5 wt% to 1 wt%, the highest non-isothermal melt-crystallization peak temperature was 132.5°C for PLLA/1%TAPH and the largest non-isothermal melt-crystallization enthalpy was 50.8 J/g for PLLA/0.5%TAPH. Further increasing TAPH's concentration causes the non-isothermal melt-crystallization peak to shift to the low-temperature side, showing that a high TAPH concentration cannot bring about better crystallization ability due to the hindrance effect of a high TAPH concentration on the migration of the PLLA molecular segment.

In the non-isothermal melt-crystallization section, the influence of a higher cooling rate on non-isothermal melt crystallization was further examined with DSC as shown in Figure 3. It is very clear that the cooling rate is an important factor that affects the non-isothermal melt crystallization of PLLA. When the cooling rate increases, the non-isothermal melt-crystallization peak of a given PLLA/TAPH shifts toward the lower temperature side. Meanwhile, the non-isothermal melt-crystallization exotherm becomes broader. Even when the cooling rate is 20°C/min, the non-isothermal melt-crystallization peak width

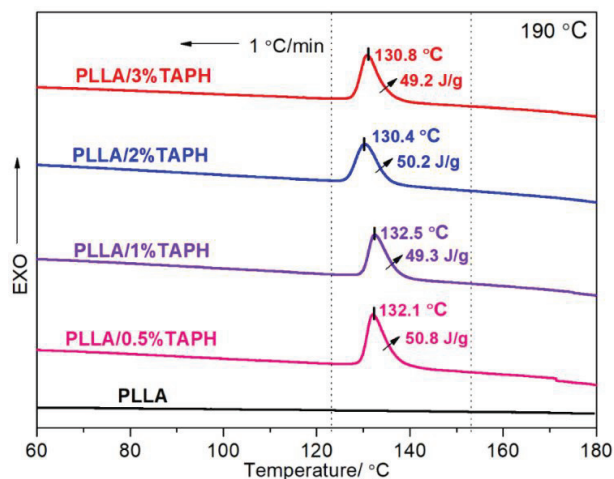


Fig. 2. DSC cooling curves of pure PLLA and PLLA/TAPH from 190°C at a rate of 1°C/min

of PLLA/TAPH exceeds 40° C, showing a poor crystallization ability and slow crystallization rate. These results indicate that an increase in cooling rate is not conducive to improving PLLA's crystallization because a high cooling rate makes crystal growth difficult, and crystallization can only be completed within a relatively wide temperature range. Similar results can be easily found in other systems based on PLLA such as PLLA/CB [36], PLLA/BAS [37], and PLLA/TBOD [38]. Additionally, as can be seen, PLLA containing a larger amount of TAPH exhibits a weaker crystallization ability, and this effect is more prominent with an increase in cooling rate. The reason for this is that a larger amount of TAPH has more negative effects on the migration of the PLLA molecular segment, resulting in a very wide melt-crystallization peak.

3.2. Non-isothermal cold crystallization

Cold crystallization is another important part of non-isothermal crystallization, and the DSC heating curves of PLLA/TAPH from room temperature to 180°C at different rates (1°C/min, 2.5°C/min, and 5°C/min) are displayed in Figure 4. For a given PLLA/TAPH, with an increasing heating rate from 1°C/min to 5°C/min, the wider and flatter non-isothermal cold-crystallization peak is located at a higher temperature, and this effect is thought to be due to thermal inertia. Through DSC

data analysis, when the heating rate is 1°C/min, the non-isothermal cold-crystallization peak temperatures for PLLA/0.5%TAPH, PLLA/1%TAPH, PLLA/2%TAPH, and PLLA/3%TAPH are 87.6°C, 86.3°C, 85.6°C, and 85.1°C, respectively, showing that the incorporation of TAPH into PLLA leads to a shift toward the low-temperature side of the non-isothermal cold-crystallization peak, which is opposite to the effect of WS₂ on PLLA's non-isothermal cold crystallization [39]. Furthermore, when the heating rate is 2.5°C/min or 5°C/min, the influence of TAPH concentration on non-isothermal cold crystallization also exhibits the aforementioned variation law apart from PLLA/1%TAPH. The reason is that a larger amount of TAPH can more rapidly induce crystallization in heating because of a higher nucleation density. In addition, it is shown in Figure 4 that the melting range of a given PLLA/TAPH after non-isothermal cold crystallization is almost independent of the heating rate used.

3.3. Melting behavior

In addition to investigating non-isothermal crystallization, the melting processes of PLLA/TAPH after non-isothermal melt crystallization and isothermal crystallization were further estimated by DSC. Figure 5 shows the effect of heating rate on PLLA/TAPH's melting behaviors after melt crystallization at a cooling rate of 1° C/min. It is clear that when the heating rate is 1°C/min and 2°C/min, there are obvious double-melting peaks in the DSC curves, indicating that a recrystallization phenomenon occurs in heating because only a single melting peak appears when further increasing the heating rate. This suggests that double-melting peaks cannot be attributed to the melting of crystals of different stability (dual morphology mechanism). Furthermore, the low-temperature side of the melting peak is attributed to the melting of primary crystallites, and the high-temperature side of the melting peak reflects the melting of crystallites formed by recrystallization in heating. Furthermore, it was observed that in comparison to PLLA/0.5%TAPH and PLLA/1%TAPH,

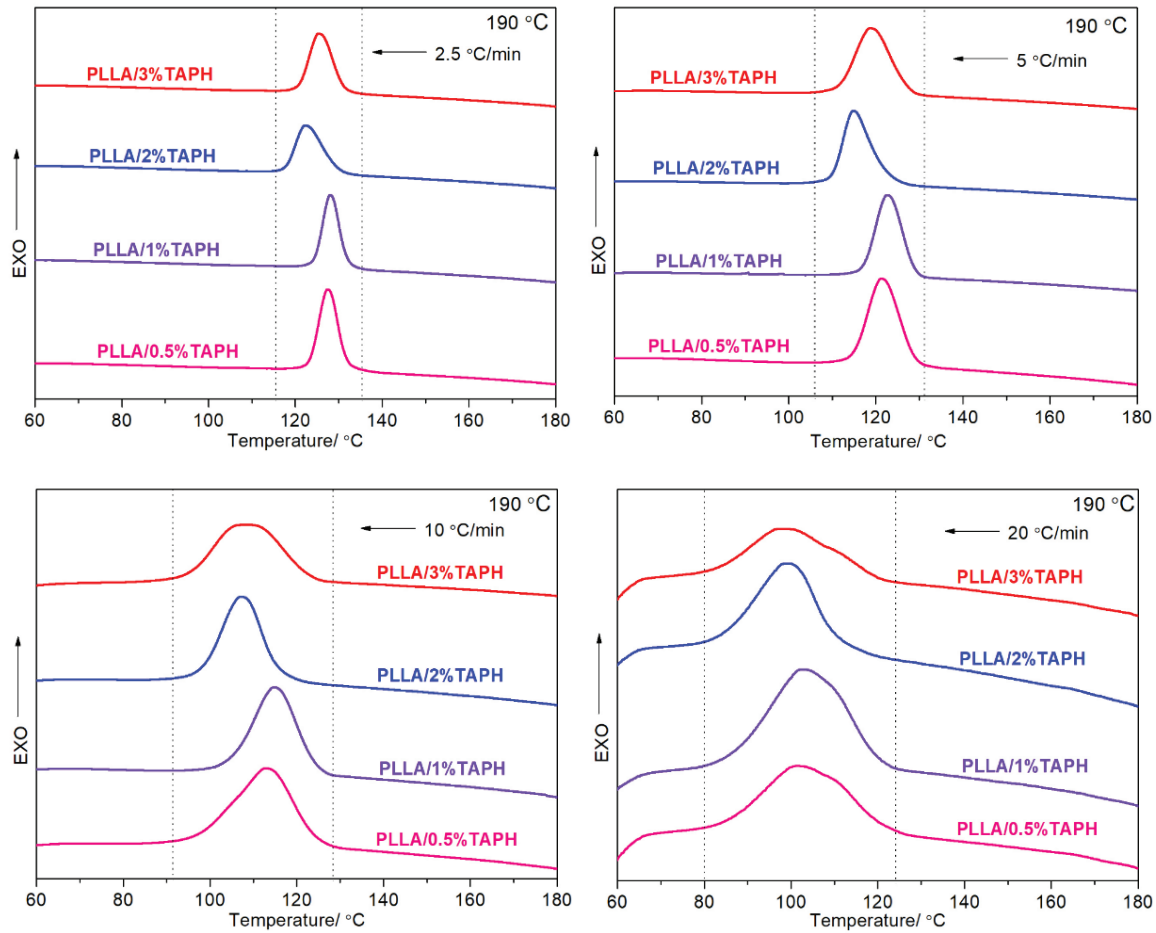


Fig. 3. DSC cooling curves of PLLA/TAPH at different rates (2.5°C/min, 5°C/min, 10°C/min, and 20°C/min)

PLLA/2%TAPH and PLLA/3%TAPH possess a larger peak area on the high-temperature side of the melting peak, and PLLA/1%TAPH has the smallest high-temperature side of the peak area. Even when the heating rate is 2°C/min, the high-temperature melting peaks of PLLA/0.5%TAPH and PLLA/1%TAPH can almost not be observed. This result must depend on the previous non-isothermal melt-crystallization behavior, because PLLA/0.5%TAPH and PLLA/1%TAPH exhibit better crystallization ability compared with PLLA/2%TAPH and PLLA/3%TAPH as shown in Figure 2, resulting in crystallization being fully performed in cooling. Additionally, with an increase in heating rate, the melting range of a given PLLA/TAPH becomes significantly wide. The reason for this is thought to be due to the effect of thermal inertia.

The crystallization of a semi-crystalline polymer usually occurs in the temperature range between glass transition temperature and melting temperature, therefore, crystallization temperature is a key index for completing crystallization, as reported in the literature [40, 41]. Figure 6 shows the melting processes of PLLA/TAPH at a heating rate of 10°C/min after full crystallization at different temperatures (110°C, 115°C, 120°C, 125°C, 130°C, and 135°C). As seen in Figure 6, when the crystallization temperature is relatively low, such as 110°C or 115°C, all DSC melting curves appear as typical double-melting peaks, indicating that a relatively low crystallization temperature cannot realize full crystallization even if the crystallization time is long enough. Furthermore, the lower the crystallization temperature is, the more obvious the high-temperature side

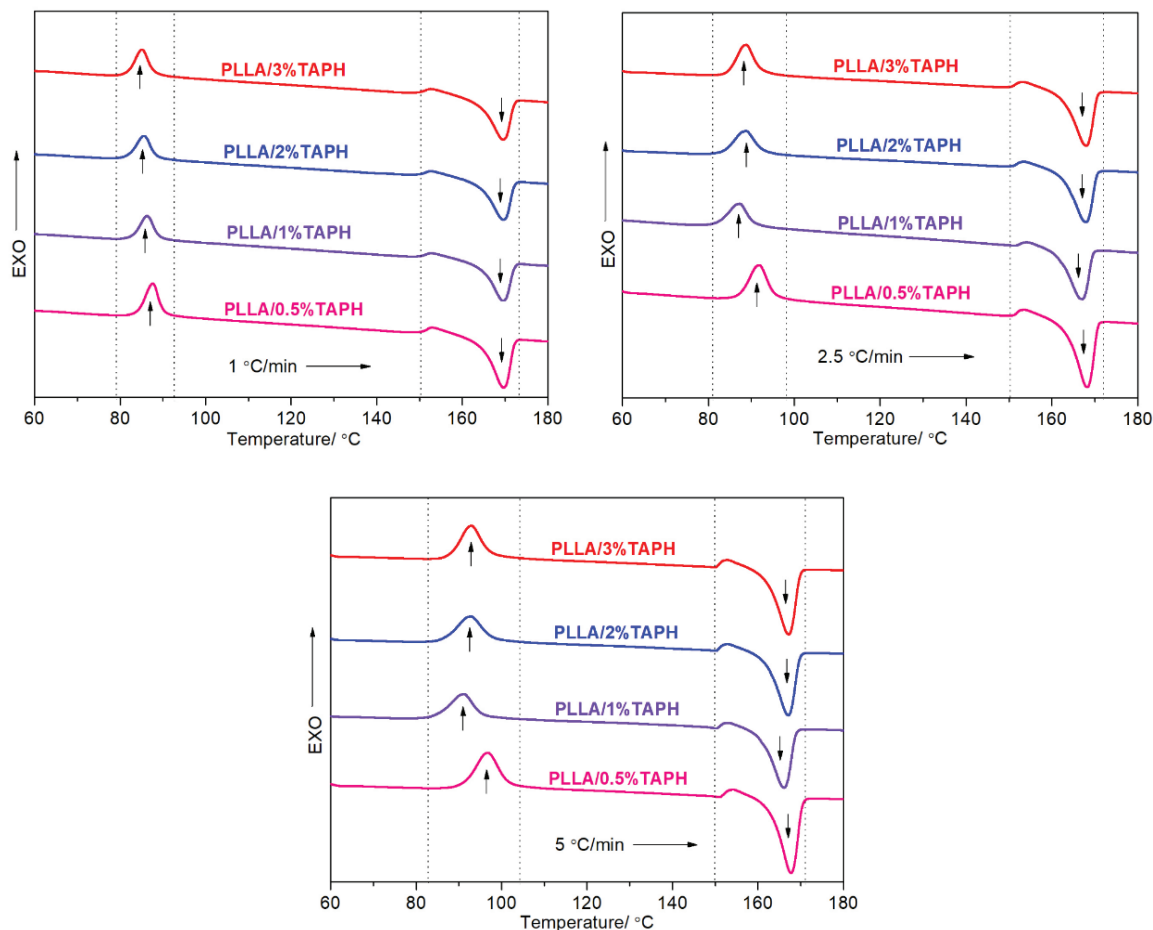


Fig. 4. DSC heating curves of PLLA/TAPH at different rates (1°C/min, 2.5°C/min, and 5°C/min)

of the melting peak becomes. When the crystallization temperature is higher than 120°C, there is only a single melting peak, and the melting peak of a given PLLA/TAPH shifts toward the higher temperature side as the crystallization temperature increases, which shows that a relatively high crystallization temperature can promote better growth in crystallites and obtain more perfect crystals. As a result, the melting of PLLA occurs at a higher temperature. Additionally, it was found that the melting temperature follows this rule: PLLA/1%TAPH < PLLA/0.5%TAPH < PLLA/2%TAPH < PLLA/3%TAPH, which is almost contrary to the results of the effect of TAPH concentration on PLLA's crystallization ability as shown in Figure 2, because PLLA/1%TAPH exhibits better crystallization ability and has a faster crystallization rate compared with the other PLLA/TAPH,

which results in crystallization being rapidly completed. As a result, the shape of the formed crystal becomes poor, and these imperfect crystals are the first to melt in heating.

3.4. Optical and mechanical properties

Among biodegradable polyesters, good transparency is an important feature of PLLA, but the introduction of additives often decreases the transparency of PLLA. Figure 7 shows the effect of TAPH and its concentration on PLLA's transparency. It can be noted that the incorporation of TAPH seriously undermines PLLA's transparency, as seen in Figure 7. When only 0.5 wt% TAPH was added into the PLLA matrix, the transparency of PLLA/0.5%TAPH decreased from 78.2% to 17.5% compared with pure PLLA, meaning that

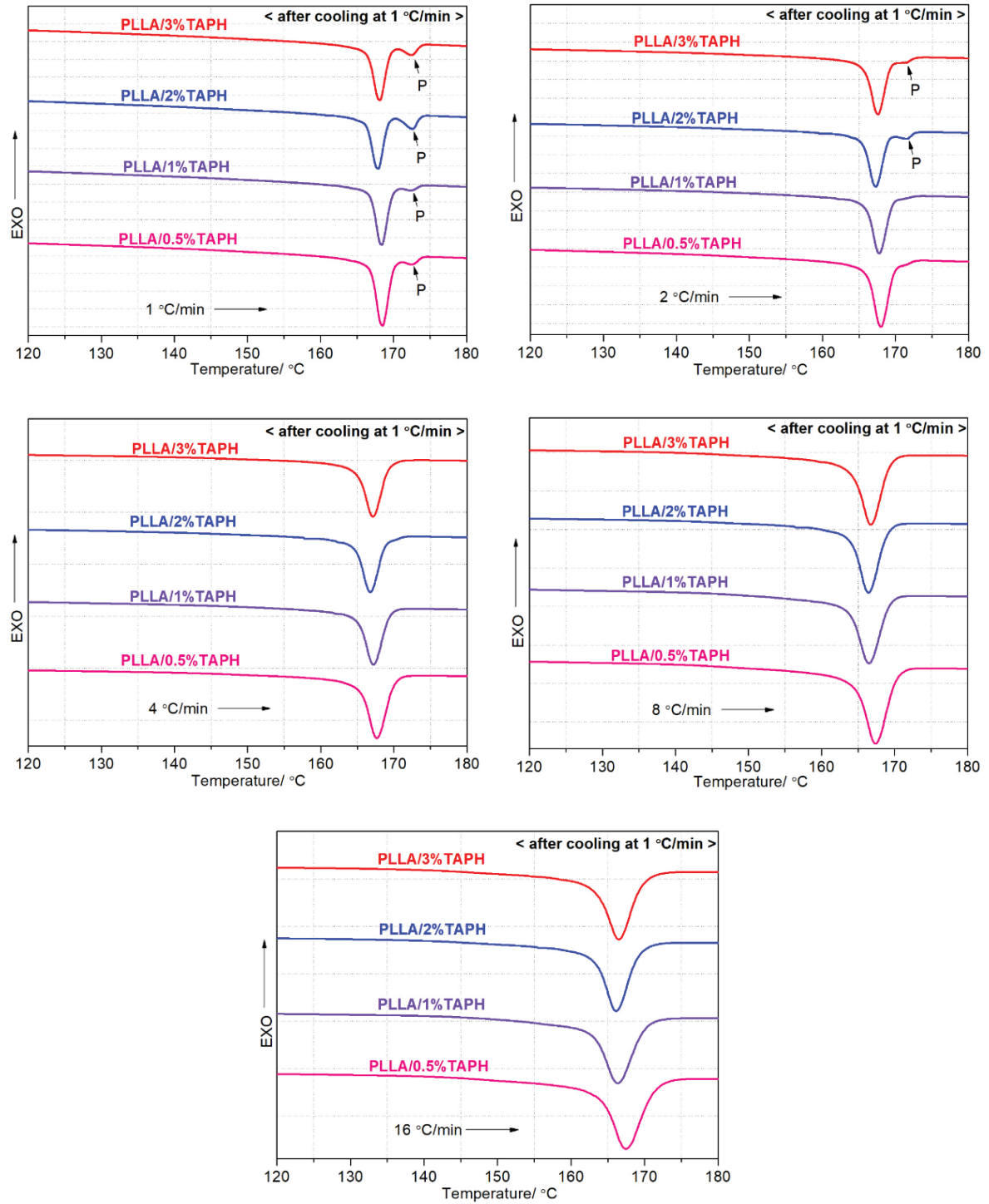


Fig. 5. Melting processes of PLLA/TAPH at different heating rates (1°C/min, 2°C/min, 4°C/min, 8°C/min, and 16°C/min) after melt crystallization

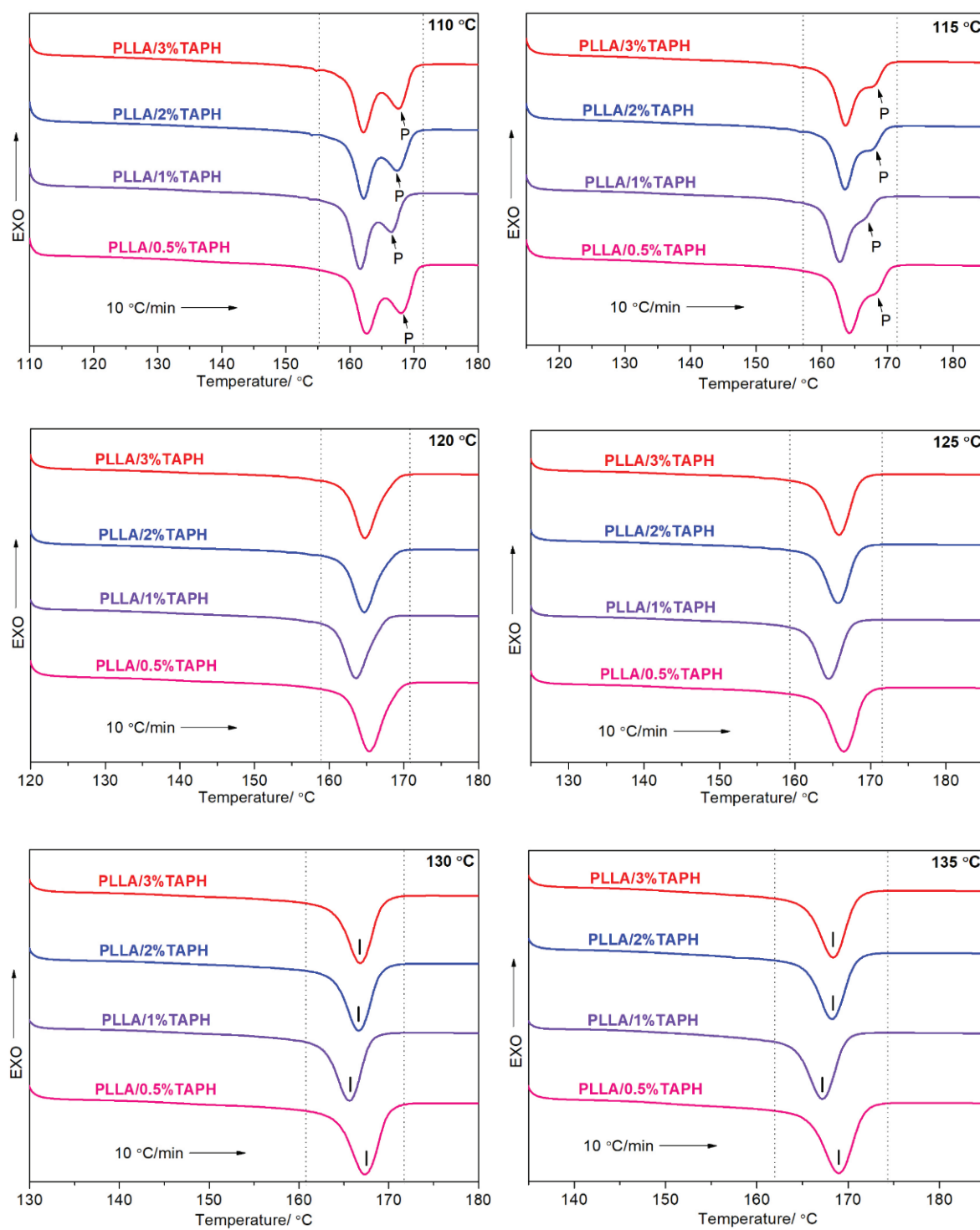


Fig. 6. DSC melting curves of PLLA/TAPH after isothermal crystallization at different temperatures for 180 min

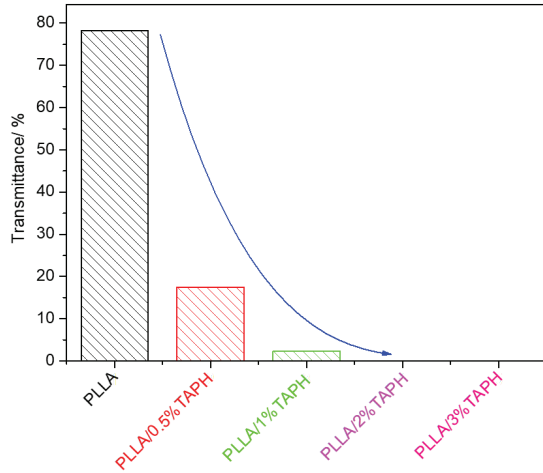


Fig. 7. Transparency of pure PLLA and PLLA/TAPH

the transparency of PLLA/0.5%TAPH was only 0.22 times that of pure PLLA. By further increasing TAPH's concentration to 1 wt%, the transparency decreased to only 2.3%, and even when TAPH's concentration in the PLLA matrix was up to 2 wt%, the transparency of PLLA was zero. According to the analysis of potential influencing factors, this serious decline in transparency is thought to be due to two main reasons. One reason is the addition of white TAPH that leads to a decline in PLLA's transparency. The other reason is that TAPH, as a nucleating agent, accelerates PLLA's crystallization during manufacturing and an increase in crystallinity can also reduce PLLA's transparency.

The tensile modulus, tensile strength, and elongation at break of pure PLLA and PLLA containing different TAPH concentrations are displayed in Figure 8. In terms of tensile strength, when TAPH concentration increased to 0.5 wt%, the tensile strength exhibited a maximum value of 83.7 MPa. When continuing to increase TAPH concentration to 2 wt%, the tensile strength decreased from a maximum value of 83.7 MPa to a minimum value of 49.3 MPa, which was still higher than the 41.7 MPa value of pure PLLA. After this, the tensile strength increased again with an increase in TAPH concentration. Similarly, PLLA/0.5%TAPH possessed the largest tensile modulus, and the tensile modulus of any PLLA/TAPH was higher than that of pure PLLA. In contrast, PLLA/0.5%TAPH

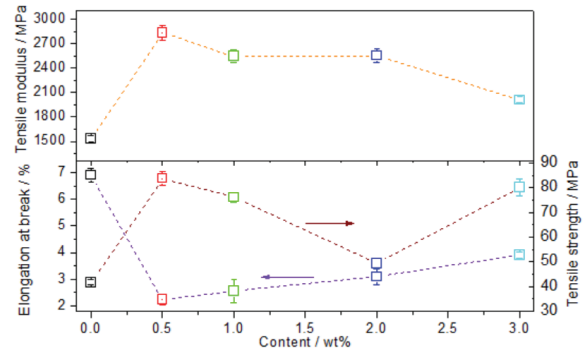


Fig. 8. Effect of TAPH loading on the mechanical properties of PLLA

had a minimum elongation at break of 2.2%, and the elongation at break of any PLLA/TAPH was lower than that of pure PLLA, although the elongation at break increased slightly as TAPH concentration increased from 0.5 wt% to 3 wt%. The effect of TAPH on elongation at break indicates that the introduction of TAPH causes PLLA to become brittle, resulting from two probable reasons. One reason is the defect caused by incomplete compatibility of PLLA with TAPH; another reason is PLLA/TAPH's higher crystallinity, which is attributed to the accelerating role of TAPH for PLLA's crystallization, because the higher the crystallinity is, the greater the brittleness is. However, a slight increase of elongation at break with an increase of TAPH loading from 0.5 wt% to 3 wt% shows the plasticizing role of TAPH for PLLA to some extent.

4. Conclusion

In this work, TAPH was used to prepare TAPH-nucleated PLLA materials. Non-isothermal melt crystallization indicated that TAPH could effectively promote PLLA's crystallization because TAPH provided a nucleation site during PLLA's entire cooling process, and TAPH, as a nucleation site for PLLA crystallization, was not affected by the temperature during cooling. However, PLLA/TAPH's crystallization ability was not entirely dependent on TAPH's concentration. In contrast, crystallization occurred at low temperatures in PLLA with high TAPH loadings (2 wt%

or 3 wt%). In addition, through analysis of crystallization peak width, the appearance of a wider crystallization peak implied that increasing the cooling rate was not conducive to PLLA's crystallization. For non-isothermal cold-crystallization behaviors, the differences in cold-crystallization peak position and shape further confirmed TAPH's nucleation effect, and these differences also depended on the heating rate during heating. The studies on PLLA/TAPH melting behavior showed that the multiple melting behaviors of PLLA/TAPH were determined by TAPH loading, non-isothermal crystallization behaviors before the melt, and isothermal crystallization behaviors before the melt. In detail, both a slow heating rate during melting and a low crystallization temperature during isothermal crystallization could result in the appearance of double-melting peaks. Furthermore, the addition of TAPH seriously destroyed PLLA's transparency, the transparency of PLLA/0.5%TAPH was only 0.22 times that of PLLA. For PLLA/TAPH's mechanical properties, the tensile modulus and tensile strength of PLLA/TAPH were enhanced when compared with pure PLLA, but pure PLLA has a higher elongation at break than any PLLA/TAPH because the introduction of TAPH caused PLLA to become brittle.

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