

The Application of *N, N'*-bis(Isonicotinic Acid) 1, 4-Naphthalenedicarboxylic Acid Dihydrazide in Biodegradable Poly(L-lactide): Crystalline Nucleation, Melting Behavior, Thermal Stability and Mechanical Properties

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Abstract: Improving the crystallization performance of poly(L-lactide) (PLLA) is necessary to adapt for various applications. In the current work, *N, N'*-bis(isonicotinic acid) 1, 4-naphthalenedicarboxylic acid dihydrazide (NAIAH) was synthesized to be firstly aimed at promoting the crystallization of PLLA, and the NAIAH-nucleated PLLA materials were prepared using PLLA as a matrix material and NAIAH as a nucleating agent, and the crystalline nucleation, melting behavior, thermal decomposition and mechanical properties of PLLA/NAIAH samples were investigated by the relevant testing instruments. The results from the non-isothermal melt-crystallization from the melt of 190°C indicated that the NAIAH could significantly accelerate PLLA's crystallization, and played an efficient heterogeneous nucleation in PLLA's crystallization. The effect of different final melting temperatures on PLLA's melt-crystallization behavior showed that a relatively low final melting temperature was beneficial for the crystallization of PLLA, and the 170°C was the optimum final melting temperature in this study. An increase of cooling rate could weaken PLLA/NAIAH's crystallization ability, but the NAIAH was still able to promote PLLA's crystallization upon the fast cooling at 50°C/min, showing a powerful crystallization accelerating effect of NAIAH. PLLA/NAIAH's melting behaviors after different crystallization conditions were affected by heating rate and crystallization temperature, and the double melting peaks appeared in melting DSC curves were assigned to melting-recrystallization. Thermal decomposition processes in air showed that the NAIAH decreased PLLA's thermal stability, but the interaction of PLLA with NAIAH had an inhibition for a drop in onset decomposition temperature. Additionally, the introduction of NAIAH dramatically reduced PLLA's tensile modulus and elongation at break.

Keywords: Poly(L-lactide), 1,4-naphthalenedicarboxylic acid, crystallization, organic nucleating agent, thermal behavior

1. Introduction

Poly(L-lactide) (PLLA) has exhibited a leading position in the present biodegradable and environmental-friendly polymers due to its renewable origin [1], excellent biodegradable and biocompatible [2], easy process [3]. Moreover, with becoming worse of the environmental problems in the past decade, PLLA must attract more attentions in both industrial production and academic research fields. Currently PLLA has been used in a diverse range of applications such as packaging materials [4, 5], automotive industry [6], medical materials [7-10], electronics [11, 12], etc. However, the heat distortion temperature of amorphous PLLA is only around 60°C [13], showing a very poor heat resistance, even this heat distortion temperature cannot meet the basic requirements of usage. Additionally, it often takes a long time to complete PLLA's molding during manufacturing to reach the terminal using temperature. Whereas both the poor heat resistance and the long molding cycle directly depend on PLLA's crystallization rate, because a fast crystallization rate can bring about the high crystallinity which improves the heat resistance and shorten the molding cycle.

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Unfortunately, as reported [14-16], PLLA suffers from a very slow crystallization rate because of its poor crystallization ability. Thereby accelerating PLLA's crystallization seems to be very significant for strengthening practical application in relevant fields. Through the exploration and comparison for many years, adding a nucleating agent is thought to be a very good way of promoting the crystallization of polymer [17, 18], because a nucleating agent can reduce the surface free energy barrier toward nucleation and induce the occurrence of crystallization; and this method has already widely applied in semi-crystalline polymers, including polyethylene terephthalate [19] and polypropylene [20, 21], to enhance their crystallization performances. Similarly, this method can also be employed in PLLA as another semi-crystalline polymer. According to the category, the nucleating agents for PLLA are divided into inorganic nucleating agents and organic nucleating agents, the typical inorganic nucleating agents have silicate [22-24], metals phenylphosphonate [25, 26] and nano oxide [27, 28]; and the organic nucleating agents mostly focus on benzoylhydrazine derivatives [29, 30], oxalamide derivatives [31, 32], humic acid derivatives [33, 34], 1H-benzotriazole derivatives [35, 36], etc. Compared to the organic nucleating agents, a serious shortcoming of the inorganic nucleating agent is its poor compatibility with PLLA matrix, and surface modification technology is used to overcome this defect, but the surface modification can reduce the nucleation effect of inorganic matter to a certain extent [37]. Additionally, the high loading of an inorganic nucleating agent may leads to poor mechanical properties of PLLA products [13]. Thus, the organic nucleating agents are growing in popularity due to the relatively better compatibility [38], excellent nucleation effect [39], and flexible regulation of molecular structure [40]. However, both the category and nucleation ability of organic nucleating agents still need to be further enhance to realize large-scale application in PLLA processing field, especially developing more new organic nucleating agent's categories is very meaningful to explore the important effect of some critical organic groups on the PLLA's crystallization and nucleation mechanism, as well as design more efficient and commercial organic nucleating agent according to the combination of molecular group. Based on the reason, the current work is aimed at introducing a new organic compound *N, N'*-bis(isonicotinic acid) 1, 4-naphthalenedicarboxylic acid dihydrazide (NAIAH) into PLLA resin, and the PLLA containing various NAIAH contents were fabricated by melt blending technology, and the properties of the PLLA/NAIAN were investigated in terms of crystalline nucleation, melting behavior, thermal stability and mechanical properties.

2. Materials and methods

2.1. PLLA and NAIAH

The 4032D PLLA in this study was supplied by Nature-Works LLC, USA. Two step reactions of acylation and amination were used to synthesis the organic nucleating agent NAIAH, and NAIAH's molecular structure is shown in Figure 1 (Fourier Transform Infrared Spectrometer (KBr) ν : 3461.8, 3002.9, 1696.5, 1654.0, 1603.9, 1582.4, 1558.3, 1514.5, 1499.7, 1457.4, 1426.4, 1408.9, 1384.1, 1347.6, 1296.6, 1258.5, 1215.3, 1140.7, 1061.4, 1035.7, 1021.1, 1003.9, 921.7, 846.8, 824.9, 780.8, 750.2, 689.6 cm^{-1} ; ^1H Nuclear Magnetic Resonance (400 MHz) δ : ppm; 11.02 (s, 1H, NH), 10.74 (s, 1H, NH), 8.82~8.84 (d, 2H, Py), 8.45~8.48 (m, 2H, Py), 7.71~7.90 (m, 3H, Naphth).

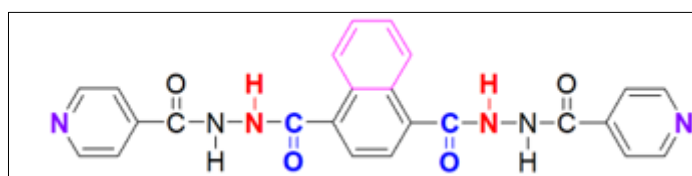


Figure 1. Molecular structure of NAIAH

2.2. Preparation of PLLA/NAIAH samples

The PLLA and modified PLLA samples were prepared by melt blending with the NAIAH loading ranging from 0 wt% to 3 wt%. First, to thoroughly remove residual water in PLLA and NAIAH, the

PLLA and NIAIAH were dried over night at 45°C under vacuum; and then the blend of PLLA containing different amount of NIAIAH (0 wt%, 0.5 wt%, 1 wt%, 2 wt%, 3 wt%) were performed on a counter-rotating mixer, and the relevant samples were designated as PLLA, PLLA/0.5%NIAIAH, PLLA/1%NIAIAH, PLLA/2%NIAIAH and PLLA/3%NIAIAH. The blending temperature was set to 190°C, and the blending time is set at 32 rpm for 5 min and 64 rpm for 5 min, respectively. Finally, all samples were hot pressed at 190°C and cool pressed at room temperature using pressure of 20 MPa to obtain the final samples with a thickness of 0.4 mm for testing.

2.3. Measurement

The crystallization promoting ability of NIAIAH on PLLA was evaluated through non-isothermal crystallization, and the non-isothermal crystallization processes of the virgin PLLA and PLLA/NIAIAH were recorded by Q2000 differential scanning calorimetry (DSC) made by TA instrument; additionally, the melting behaviors of PLLA/NIAIAH under different conditions were also performed on the Q2000 DSC. Before DSC testing, the flow rate of nitrogen atmosphere was firstly set to 50 mL/min, and then the temperature and heat flow were calibrated using an indium standard, as well as all testing samples were heated to 190 °C for 5 min to eliminate thermal history to ensure the test at the same level. After that, the detailed testing procedures were performed. The thermal decomposition behaviors of the virgin PLLA and PLLA/NIAIAH in the air were determined by Q500 thermal gravimetric analyzer (TGA) with 60 mL/min flowing air, and the testing temperature covers the range of 40~650°C at a heating rate of 5°C/min. A D&G DX-10000 electronic tensile tester with 1 mm/min stretching speed was used to test the effects of NIAIAH on PLLA's mechanical properties, and the dimension of the tested sample was 25 mm×4 mm×0.5 mm.

3. Results and discussions

3.1. Melt-crystallization behavior

To evaluate NIAIAH's nucleation ability for PLLA's crystallization, the melt-crystallization processes of the virgin PLLA and PLLA/NIAIAH were firstly examined. Figure.2 is the melt-crystallization DSC curves of the virgin PLLA and PLLA/NIAIAH in different weight fractions of NIAIAH from the melt of 190°C at a cooling rate of 1 °C/min. For all PLLA/NIAIAH, the obvious and sharp non-isothermal melt-crystallization peaks appear in DSC cooling curves compared with that of the virgin PLLA, which indicates that the NIAIAH has an evident crystallization accelerating ability for the PLLA's crystallization in the same way as other nucleating agents [41, 42], this mainly because that the incorporation of NIAIAH as a heterogeneous nucleus instantaneously increases PLLA's nucleation density, resulting in the efficient formation of crystal in cooling due to the fast nucleation rate and excellent migration and rearrangement of PLLA molecular chains. In contrast, the virgin PLLA cannot form the nucleus *via* homogeneous nucleation of PLLA itself so that the crystallization cannot occur in cooling, because the polymer's crystallization often includes two stages of nucleation and crystal growth [43], if the nucleus could not form, the crystal growth cannot occur correspondingly. As a result, the virgin PLLA's non-isothermal melt-crystallization peak can almost not be observed in cooling DSC curve. Additionally, the Figure 2 also displays the effect of NIAIAH loading on PLLA's non-isothermal melt-crystallization behavior, it is clear that the non-isothermal melt-crystallization peak shifts toward the higher temperature with increasing of NIAIAH loading, further confirming the powerful nucleation ability of NIAIAH, because the role of nucleating agent is to induce the crystallization to occur in the higher temperature region. With increasing of loading from 0.5 wt% to 3 wt%, the onset non-isothermal melt-crystallization temperature, the non-isothermal melt-crystallization peak temperature and non-isothermal melt-crystallization enthalpy increase from 137.1°C, 133.1°C and 48.0 J/g to 139.6°C, 135.9°C and 50.6 J/g, respectively; and the difference between the onset non-isothermal melt-crystallization temperature and the non-isothermal melt-crystallization peak temperature decreases from 4.0°C to 3.7°C, which means that the non-isothermal melt-crystallization peak gradually become narrow, indicating that PLLA's overall crystallization rate is accelerated by a higher NIAIAH loading.

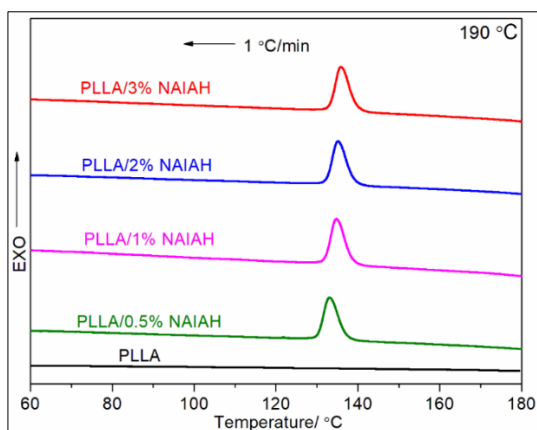


Figure 2. Melt-crystallization DSC curves of the virgin PLLA and PLLA/NAlAH samples at a cooling rate of 1 °C/min

In the study of non-isothermal melt-crystallization, the final melting temperature (T_f) is an important factor for affecting the crystallization process of nucleated semi-crystalline polymers as reported [35, 44]. Usually, for an organic nucleating agent, the T_f can directly determine the solubility of organic nucleating agent in polymer matrix and nucleation density, and eventually the non-isothermal melt-crystallization behavior was affected by T_f via the aforementioned two factors of the solubility and nucleation density. On one hand, the nucleation density depends on the amount of undissolved organic nucleating agent; however, on the other hand, the dissolved organic nucleating agent can enhance compatibility of PLLA with an organic nucleating agent and intermolecular interaction to some extent. Thus, this competitive effect leads to a complexed crystallization behavior. Figure 3 is the non-isothermal melt-crystallization DSC curves of PLLA/NAlAH from the different T_f at a cooling rate of 1 °C/min. Through the comparative analysis of DSC curves, it is observed that a lower T_f can cause the crystallization occur at a higher temperature, suggesting that the undissolved NAlAH plays a more important role in PLLA's crystallization comparing with the effect of enhancement of interaction.

The aforementioned DSC results confirm the advanced crystallization accelerating ability of NAlAH as a heterogeneous nucleating agent, and that, in comparison to other T_f , the T_f of 170 °C makes the PLLA/NAlAH possess a more powerful crystallization ability, but the cooling rate of 1 °C/min is too slow to meet the requirements of industrial production. Thus, investigating on the non-isothermal melt-crystallization behaviors of NAlAH-nucleated PLLA at a higher cooling rate is very necessary. Figure 4 shows the non-isothermal melt-crystallization DSC curves of PLLA/NAlAH from the optimum final melting temperature of 170 °C at various cooling rates from 10 °C/min to 50 °C/min. For a given PLLA/NAlAH, it is clear that, with increasing of cooling rate, a non-isothermal melt-crystallization peak with location of lower temperature and a greater width appears in the DSC curve because of the lagging response of PLLA segments motion to action frequency and rate of temperature variability, which causes the crystallization to be delayed during cooling. However, all PLLA/NAlAH still exhibit the obvious melt-crystallization peaks even upon fast cooling at 50 °C/min, evidencing that NAlAH is a high-efficient organic nucleating agent for PLLA's crystallization again. This result is very beneficial to the rapid molding of PLLA materials with moderate crystallinity. In addition, it should be noted from Fig.4 that, upon a given cooling rate, the effects of NAlAH loading on PLLA's non-isothermal melt-crystallization process of is almost irrelevant to the cooling rate, that is, the non-isothermal melt-crystallization peak still moves toward the high temperature side with an increase of NAlAH loading.

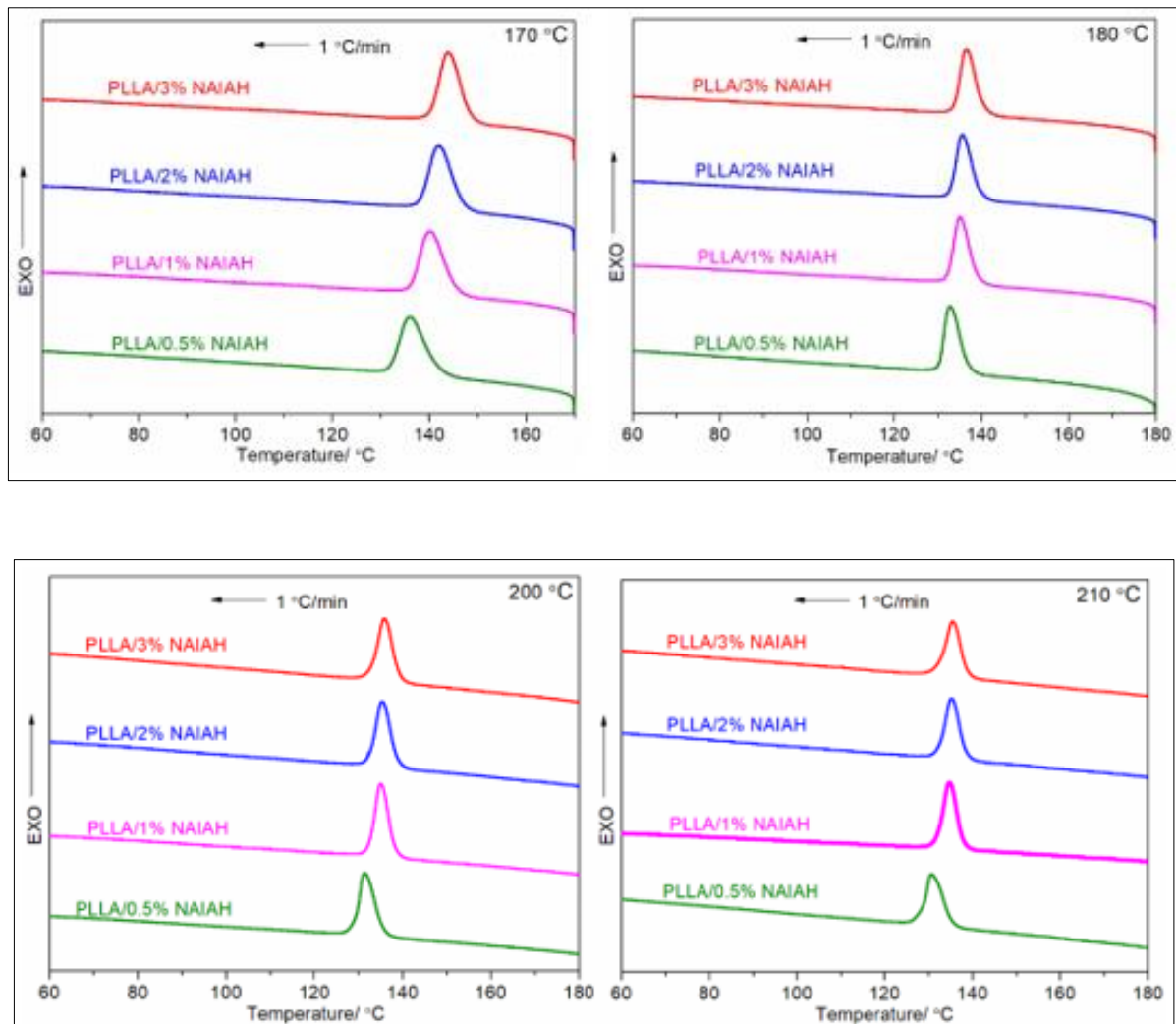
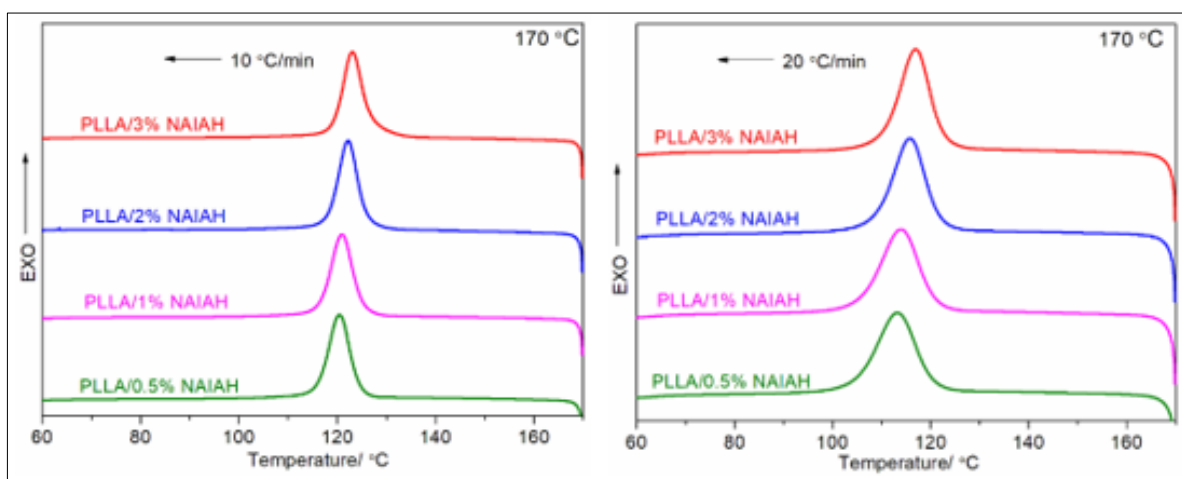


Figure 3. Melt-crystallization DSC curves of PLLA/NAIAH samples from the different T_f at the cooling rate of 1°C/min



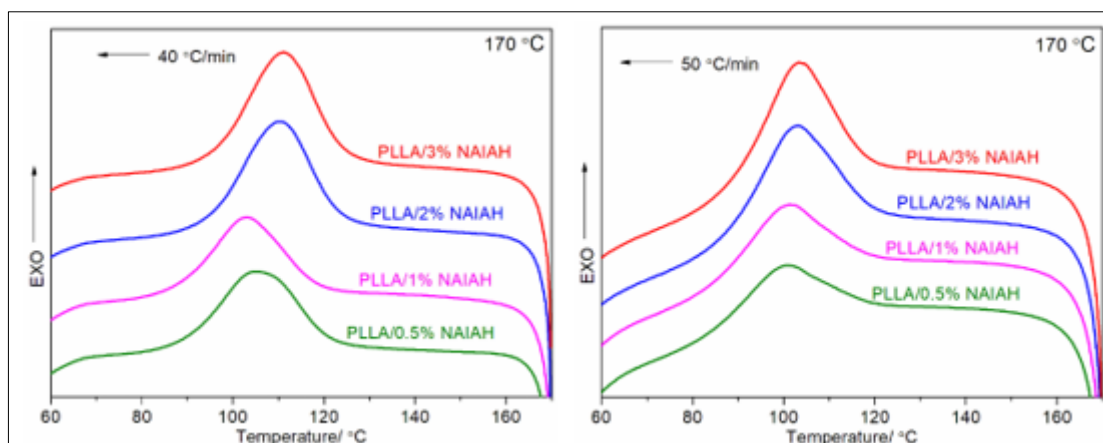
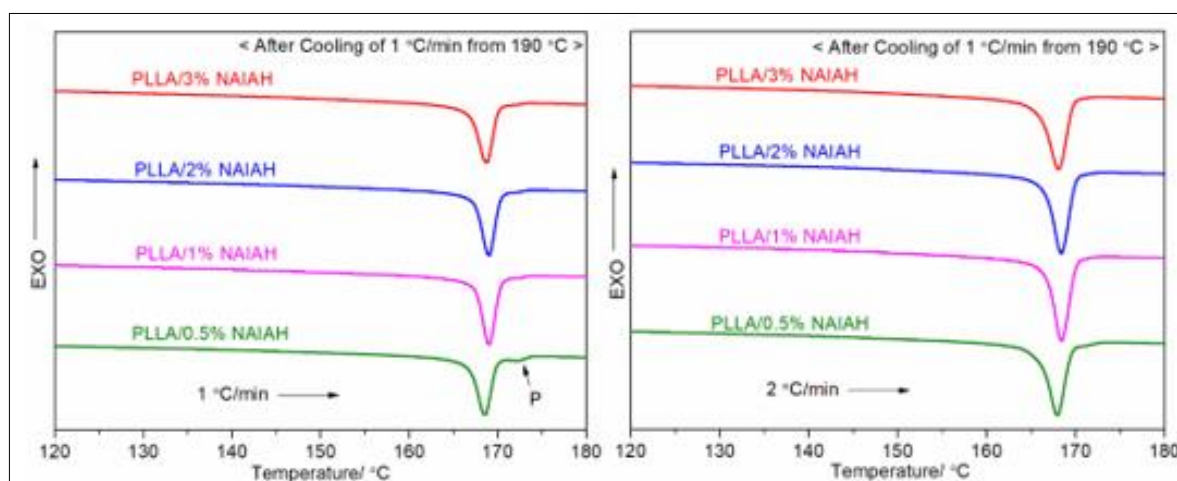


Figure 4. Melt-crystallization DSC curves of PLLA/NAIAH samples at various cooling rates

3.2. Melting behavior

Figure 5 is the DSC curves of PLLA/NAIAH's melting processes at various heating rates after non-isothermal melt-crystallization upon cooling of 1°C/min. For a given PLLA/NAIAH, it is obvious that the melting peak becomes wider with an increase of heating rate due to the thermal inertia, but a given PLLA/NAIAH's melting peak temperature is almost independent of the heating rate, indicating that the melting behavior belongs to the melt of crystals formed in previous cooling, not the crystals formed in heating, because the same cooling rate and NAIAH loading can result in the same crystallization behavior in cooling. When the heating rate is 1 °C/min, differing from the other PLLA/NAIAH, the PLLA/0.5%NAIAH exhibits the double melting peaks in melting DSC curve, suggesting that the PLLA/0.5%NAIAH cannot complete the crystallization after non-isothermal melt-crystallization upon cooling of 1°C/min, and there exist new crystal formed in heating, but the high-temperature melting peak is very faint comparing with the low-temperature melting peak, meaning that the amount of the second crystallization is very few. Through the analysis of melting process, this behavior of these double melting peaks is assigned to melting-recrystallization [45]. Upon a given heating rate, the melting peak shifts to the high-temperature side with increasing of NAIAH loading, showing that crystals are more perfect, because, for PLLA containing a higher NAIAH loading, the crystallization occurs in a higher temperature region, under this circumstance, crystals can be grown more fully due to the excellent migration and mobility of PLLA molecular chains in high temperature region. This result effectively reflects the aforementioned non-isothermal melt-crystallization DSC results.



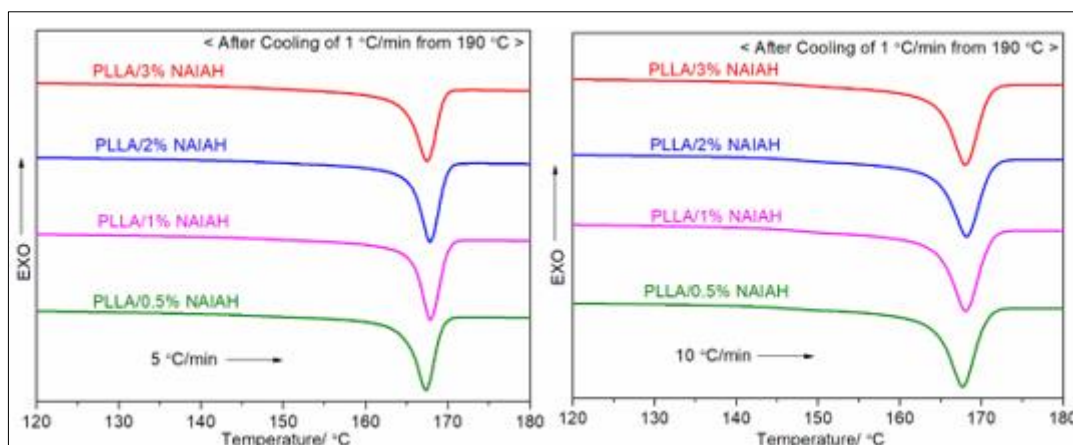
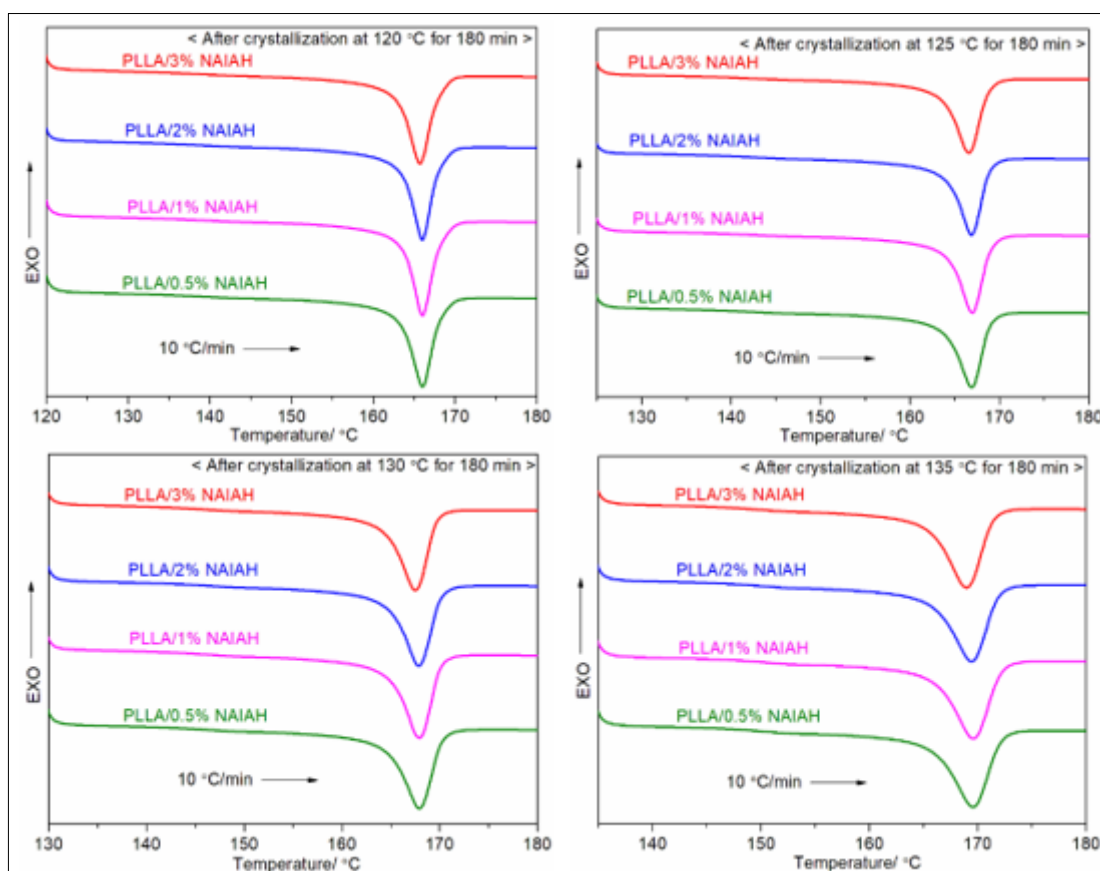


Figure 5. Melting behavior of PLLA/NAIAH samples at different heating rates after melt-crystallization

The melting behaviors of PLLA/NAIAH after isothermal crystallization at different crystallization temperatures were also investigated by DSC, and Figure 6 displays the DSC curves of PLLA/NAIAH at a heating rate of 10°C/min after adequately crystallization. It is clear that any PLLA/NAIAH has only one melting peak in the DSC curve, and that an increase of crystallization temperature leads to the melting peak's shift to the high-temperature side. When the crystallization temperature is 140°C, the melting peak temperatures of all PLLA/NAIAH are higher than 170°C, implying that the crystallization temperature of 140°C and crystallization time of 180 min make PLLA form very perfect crystal.



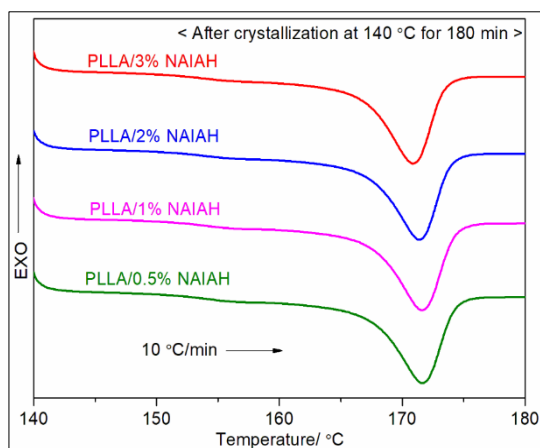


Figure 6. DSC curves of PLLA/NAlAH samples at the heating rate of 10°C/min after isothermal crystallization at different crystallization temperatures for 180 min

3.3. Thermal stability

The usage temperature range of any product must depend on its thermal stability. For PLLA/NAlAH materials, the introduction of NAlAH must influence PLLA's thermal decomposition process and behavior. Figure 7 is the TGA curves of the virgin PLLA and PLLA/NAlAH in the temperature range from 40 to 650°C at a heating rate of 5°C/min. As shown in Figure 7, all PLLA/NAlAH as the virgin PLLA have only one stage with rather similar decomposition trend, indicating that the addition of NAlAH cannot change the thermal decomposition profile of PLLA in this study, which may be thought to be due to a relative small amount of NAlAH in PLLA matrix. In addition, Figure 7 shows that this thermal decomposition stage occurs in the temperature range from 275 to 400°C, resulting from the chain scissions, loss of ester groups and subsequent combustion decomposition. Though the effect of NAlAH on PLLA's thermal decomposition profile is negligible, the addition of NAlAH reduces PLLA's onset thermal decomposition temperature (T_{od}), meaning the decline of thermal stability. Specifically the T_{od} appears at 341.3°C, 336.7°C, 336.2°C, 330.8°C and 332.1°C for the virgin PLLA, PLLA/0.5%NAlAH, PLLA/1%NAlAH, PLLA/2%NAlAH and PLLA/3%NAlAH, the data analysis of T_{od} shows that there is no a marked drop in T_{od} with increasing of NAlAH loading, and the maximum difference is only 10.5°C, even the T_{od} of PLLA/3%NAlAH is higher than that of the PLLA/2%NAlAH, the reason is that there exists the interaction between PLLA and NAlAH in PLLA/NAlAH systems, and this interaction can further enhance as NAlAH loading increases in PLLA matrix, but a larger amount of NAlAH must decrease the T_{od} of NAlAH-nucleated PLLA due to the low thermal decomposition temperature of NAlAH itself. Under this circumstance, the T_{od} depends on the synergistic effects of the interaction between NAlAH and PLLA, as well as NAlAH loading.

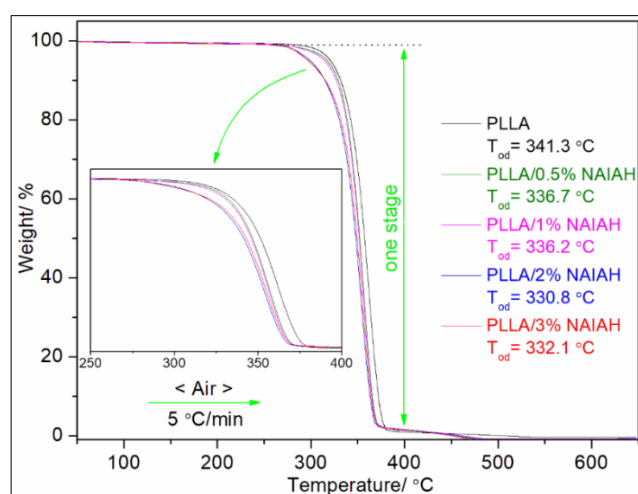


Figure 7. Thermal decomposition TGA curves of the virgin PLLA and PLLA/NAlAH samples in air

3.4. Mechanical properties

The effects of NAI AH on PLLA's mechanical properties were further studied by the electronic tensile tester, and Figure 8 presents the elongation at break, tensile strength and tensile modulus of the virgin PLLA and PLLA/NAIAH. The elongation at break decreases with NAI AH loading increasing, and shows a minimum value of 4.5 at 2 wt% NAI AH loading comparing with the 6.9% of the virgin PLLA, then the elongation at break slightly increases as NAI AH loading further increases. Overall, the presence of NAI AH decreases PLLA's elongation at break, two probable reasons are used to explain this result, the one reason is that the addition of NAI AH must give rise to some defects in PLLA matrix comparing with the virgin PLLA, and these defects can significantly accelerate PLLA/NAIAH's break during tension test; another reason is that the NAI AH can promote PLLA's crystallization, and the enhancement of crystallinity can causes the modified PLLA materials to become brittle. In contrast to the elongation at break, the tensile strength firstly increases with increasing of NAI AH loading and has the maximum value of 48.0 MPa at 0.5 wt% NAI AH loading, and then continuously decreases with further increasing of NAI AH loading, the tensile strength of the PLLA/3% NAI AH exhibits the minimum value of 35.0 MPa. Additionally, the introduction of NAI AH seriously reduces the tensile modulus of PLLA as seen in Figure 8, and the influence of NAI AH loading on the tensile modulus is irregular.

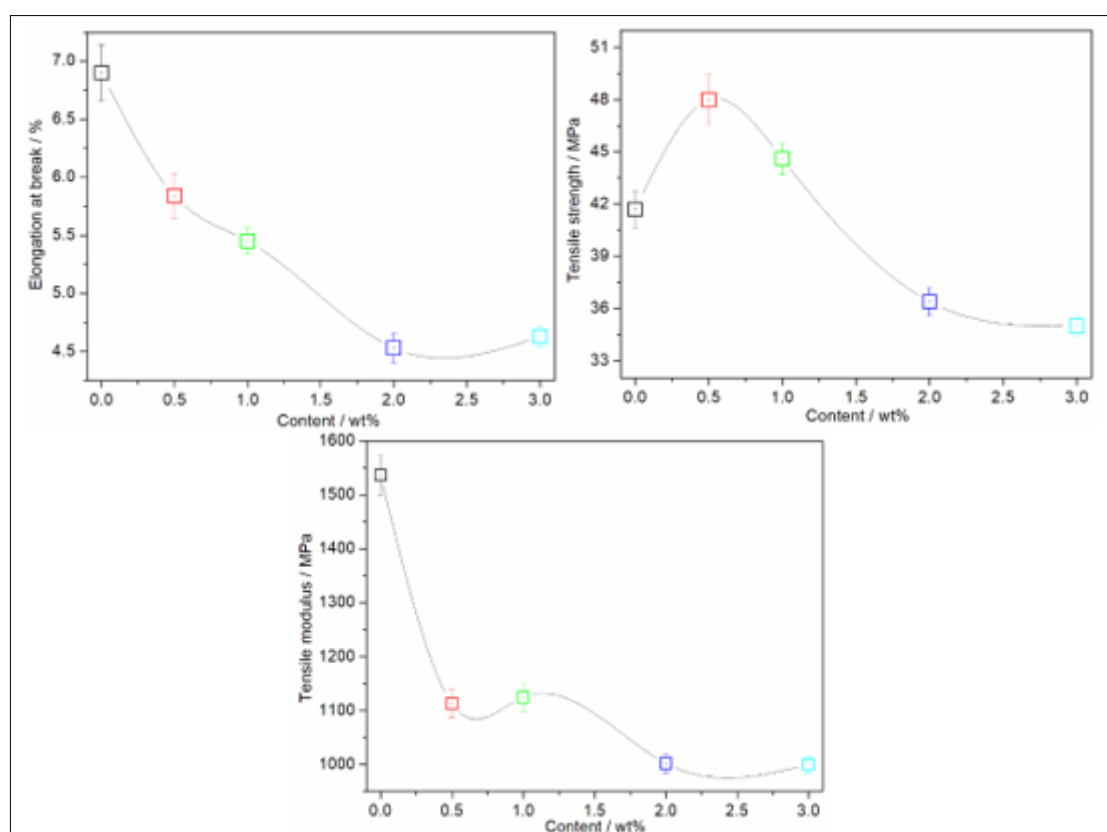


Figure 8. Mechanical properties of the virgin PLLA and PLLA/NAIAH samples

4. Conclusions

This work was the first to use NAI AH as a new organic nucleating agent to improve PLLA's crystallization. The non-isothermal melt-crystallization from the melt of 190°C at a cooling rate of 1°C/min indicated that NAI AH could be used as an effective site of heterogeneous nucleation to promote PLLA's crystallization comparing with the virgin PLLA. What is more, increasing NAI AH loading could further enhance PLLA's crystallization ability, with increasing of NAI AH loading from 0.5 wt% to 3wt%, the onset non-isothermal melt-crystallization temperature, the non-isothermal melt-crystallization peak temperature and non-isothermal melt-crystallization enthalpy increased from



137.1°C, 133.1°C and 48.0 J/g to 139.6°C, 135.9°C and 50.6 J/g, respectively. For non-isothermal melt-crystallization, the T_f was another key factor for PLLA's crystallization *via* affecting the amount of the undissolved NAlAH and intermolecular interaction of PLLA with NAlAH, and the PLLA/NAlAH exhibited the better crystallization ability with decreasing of T_f in this study, that is, compared to the other T_f , the T_f of 170°C was more conducive to crystallization. Moreover, when the T_f was 170°C, the influence of the cooling rate on crystallization behavior showed that the NAlAH could still accelerate PLLA's crystallization upon a very fast cooling rate such as 40°C/min or 50°C/min, confirming the powerful crystallization accelerating effect of NAlAH. On one hand, the melting behaviors after non-isothermal melt-crystallization and isothermal crystallization were affected by the heating rate and crystallization temperature; on the other hand, these melting behaviors also reflected the nucleation role of NAlAH in PLLA matrix. Meantime, the result of the double melting peaks was thought to be because of the melting-recrystallization. The NAlAH could not change PLLA's thermal decomposition profile, but the NAlAH could decrease PLLA's thermal stability in air, whereas the intermolecular interaction of PLLA with NAlAH tried to prevent a decrease in thermal stability. For the mechanical properties, in general, the presence of NAlAH weakened the mechanical properties due to the crystallization and existence of NAlAH.

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