

# Nucleation, Melting Behaviour and Mechanical Properties of Poly(L-lactic acid) Affected by The Addition of N, N'-Bis(benzoyl) Suberic Acid Dihydrazide

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## ABSTRACT

A new category of nucleating agent for poly(L-lactic acid) (PLLA) was developed. An organic nucleating agent; N,N'-bis(benzoyl) suberic acid dihydrazide (NA) was synthesized from benzoyl hydrazine and suberoyl chloride which was deprived from suberic acid *via* acylation. The nucleation, melting behaviour and mechanical properties of the PLLA containing NA were investigated. NA showed excellent nucleating effects on PLLA crystallization. Compared to the neat PLLA, with the addition of 0.8 % NA, the crystallization temperature ( $T_c$ ) increase from 105.88 °C to 125.57 °C and the crystallization enthalpy ( $\Delta H_c$ ) increase from 1.379 J g<sup>-1</sup> to 31.63 J g<sup>-1</sup> at a cooling rate of 1 °C min<sup>-1</sup> from melt. In the presence of NA, the melting behaviour of PLLA was affected significantly, and a double-melting peak resulted during melting-recrystallization. The tensile strengths and tensile modulus increase with the increase of NA content and possesses a maximum value for the critical NA loading of 0.8 %. However, the elongations at break of the samples decreased significantly.

## KEYWORDS

Poly (L-lactic acid), crystallization, melting behaviour, benzoyl hydrazine.

## 1. Introduction

With the increasing public attention to environmental problems, research of biodegradable polymers has gained considerable momentum in recent years<sup>1-3</sup>. Usually, PLLA is produced from renewable resources such as maize, potato, and so on<sup>4</sup>, generally with lower energy consumption than synthetic polymers. Biopolymer are also generally non-toxic to the environment<sup>5</sup>. However, until now, PLLA still has some disadvantages. For instance, slow crystallization rate, low crystalline degree and poor heat resistance of PLLA has restricted its practical applications. Thus, it is necessary to improve PLLA to make it fully competitive with commercial thermoplastics.

Usually, the most viable method of increasing the overall crystallization rate is to use a nucleating agent. Talc is often chosen as a nucleating agent for PLLA. It has been shown that talc nucleates the crystallization of polymers through an epitaxial mechanism<sup>6</sup>. Kolstad studied the crystallization behaviour and the morphology of poly (L-lactide-co-meso-lactide) and poly (L-lactide-co-meso-lactide)/Talc composites<sup>7</sup>. His work has shown that there is a strong increase in nucleation density with the addition of talc in poly (L-lactide-co-meso-lactide). Tianyi's work showed that the overall crystallization rate of PLLA increased with an increasing content of talc<sup>8</sup>. Although a large amount of work has been done to improve the crystallization of PLLA by addition of inorganic fillers, inorganic fillers are not always the most efficient when compared with chemical nucleating agents<sup>9</sup>.

Thus, in this study, we use an advanced route to synthesis N, N'-bis(benzoyl) suberic acid dihydrazide(NA) with high yield and shorter reaction time. PLLA/NA samples were prepared by melt blending and a hot-press forming process. The nucleating effect of NA on PLLA was evaluated. The melting behaviour and mechanical properties of the materials were examined.

## 2. Experimental

Poly(L-lactic acid) (PLLA) was purchased from Nature Works LLC, USA. The other materials used in this study were of analytical grade (AR). Benzoyl hydrazine and Suberic acid were procured from Beijing Chemical Reagents Company and Chengdu Kelong Chemical Reagents Company respectively. N, N-dimethylacetamide, thionyl dichloride and pyridine were procured from Mianyang Rongshen Chemical Reagents Company.

### 2.1. Synthesis of N, N'-bis(benzoyl) Suberic Acid Dihydrazide (NA)

N, N'-bis(benzoyl) suberic acid dihydrazide was prepared as shown in Fig. 1: 0.035 mol suberic acid, 50 mL thionyl dichloride in the presence of N, N-dimethylacetamide as catalyst were mixed, and the mixture was heated up to 80 °C, and held at 80 °C for 12 h with stirring. After cooling to room temperature and evaporation of thionyl dichloride in vacuum, the residue was suberoyl chloride.

Benzoic hydrazide and 50 mL N, N-dimethylacetamide were mixed, and the mixture was purged under a nitrogen atmosphere. Suberoyl chloride was added slowly into the mixture, followed by the addition of pyridine, and the mixture was heated up to 60 °C, and held at 60 °C for 2 h with stirring.

The reaction mixture was poured into 300 mL water and stirred, followed by filtrating. The crude product obtained was washed with 300 mL water four times at room temperature, and then washed with 300 mL methanol at 55 °C to eliminate raw materials and by-products. The resulting product was dried in vacuum at 65 °C. IR (KBr) $\nu$ : 3390, 3215, 2930, 2854, 1691, 1647, 1604, 1574, 1498, 1468, 1415, 1321, 1245, 1150, 794, 692, 640 cm<sup>-1</sup>; <sup>1</sup>H NMR (DMSO, 500 MHz)  $\delta$ : ppm; 10.29 (s, 1H, NH), 9.85 (s, 1H, NH), 7.48~7.88 (m, 5H, Ar), 2.18~2.21 (t, 2H, CH<sub>2</sub>), 1.56~1.59 (t, 2H, CH<sub>2</sub>), 1.35~1.36 (d, 2H, CH<sub>2</sub>).

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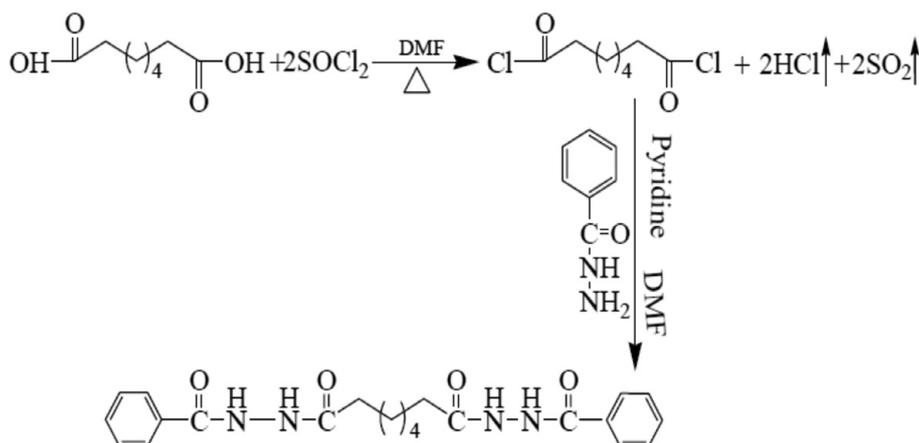


Figure 1 Synthesis of *N,N'*-bis(benzoyl) suberic acid dihydrazide.

## 2.2. Preparation of PLLA/NA Samples

PLLA was dried overnight at 50 °C under vacuum to remove residual water. Blending of PLLA and dried NA was performed on a counter-rotating mixer with a rotation speed of 32 rpm for 5 min, then at 64 rpm for 5 min. The processing temperature was set at 185 °C. Products were hot pressed at 180 °C under 20 MPa for 3 min to prepare sheets with a thickness of approximately 0.4 mm. The sheets were then cooled to room temperature by being compressed at room temperature under 20 MPa for 10 min. All the samples for crystallization studies were cut from these films.

## 2.3. Characterization

### 2.3.1. Differential Scanning Calorimeter (DSC)

The non-isothermal crystallization behaviour of PLLA was measured by DSC Q2000 (TA Instruments-Waters LLC, USA). The temperature and heat flow at different heating rate were calibrated using an indium standard. The sample was heated to 190 °C and maintained at that temperature for 5 min to make sure that the polymer crystals were completely melted. The samples were then cooled from the melt state to 20 °C at different cooling rates (1, 2, 3, 10 °C min<sup>-1</sup>). Lastly, the samples were reheated to 190 °C at the heating rate of 10 °C min<sup>-1</sup> to observe the melting behaviour. The equilibrium melting temperature ( $T_m^0$ ) was measured as follows: the sample was heated to 190 °C in heat table and maintained at that temperature for 5 min. The sample was then quenched from melt to the crystallization temperature  $T_c$  (100, 105, 110, 115, 120 °C) and held at that temperature for at least 60 min to ensure complete crystallization. The samples were then transferred to the DSC Q2000 instrument and heated at the heating rate of 10 °C min<sup>-1</sup> to record the melt endotherm.

### 2.3.2. Wide Angle X-ray Diffraction (WAXD)

WAXD experiments were performed on a diffractometer (D/MAX2550, Rigaku, Japan) using Cu  $K_\alpha$  radiation (wavelength, 1.54 Å) at room temperature in the range of  $2\theta = 5\text{--}50^\circ$  with scanning rate of 2 ° min<sup>-1</sup>.

### 2.3.3. Tensile Testing

Dumbbell-shaped tensile test specimens with effective dimensions of 25 mm × 6 mm × 1.0 mm were prepared by pneumatic-controlled impact shaping machine. Normal tensile tests were conducted on a D&G DX-10000 electronic tensile tester at the speed of 50 mm min<sup>-1</sup> at room temperature. The tensile strength, elastic modulus and elongations at break were obtained by averaging over five specimens.

## 3. Results and Discussion

### 3.1. Nucleating Effect of NA

It is very important to investigate non-isothermal crystallization to obtain the information useful for industrial applications of PLLA. Figure 2 shows the DSC curves of the non-isothermal crystallization from melt. As seen in Fig. 2, upon cooling at a rate of 1 °C min<sup>-1</sup>, the crystallization peak of PLLA can almost not be detected. This illustrates the very slow crystallization of neat PLLA. With the addition of NA, the crystallization peak appears in the DSC cooling curve. Compared to the neat PLLA, addition of NA leads to a shift of the crystallization peak to higher temperature indicating an increase in the crystallization temperature. In addition, the crystallization peak of PLLA containing NA becomes much sharper in the cooling process. This result shows that NA can serve as a nucleating agent for the crystallization and increases the overall crystallization rate of PLLA. Usually, the higher the temperature of the crystallization peak, the greater the nucleating effect on PLLA crystallization is. This results from the earlier formation of crystal nucleation during the cooling process. Upon cooling rate at a rate of 1 °C min<sup>-1</sup>, as seen in Table 1, the crystallization temperature ( $T_c$ ) is dependent on NA content and is highest upon the addition of 0.8 % NA. Compared to neat PLLA, with the addition of 0.8 % NA, the crystallization temperature ( $T_c$ ) increase from 105.88 °C to 125.57 °C and the crystallization enthalpy ( $\Delta H_c$ ) increase from 1.379 J g<sup>-1</sup> to 31.63 J g<sup>-1</sup>.

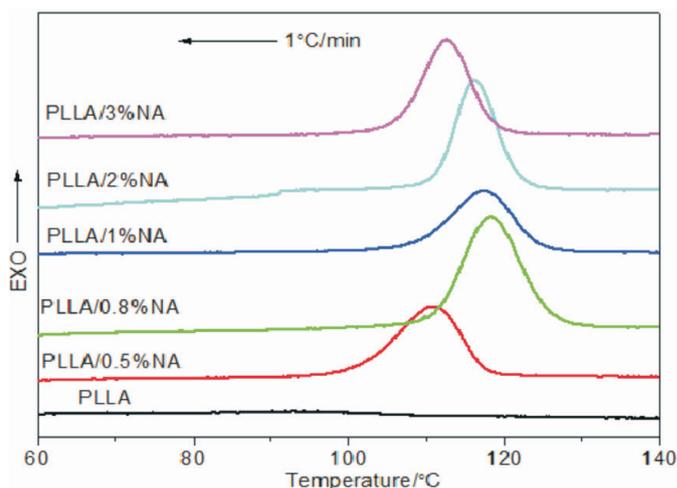


Figure 2 DSC of PLLA and PLLA/NA crystallized from melt at a cooling rate of 1 ° min<sup>-1</sup>.

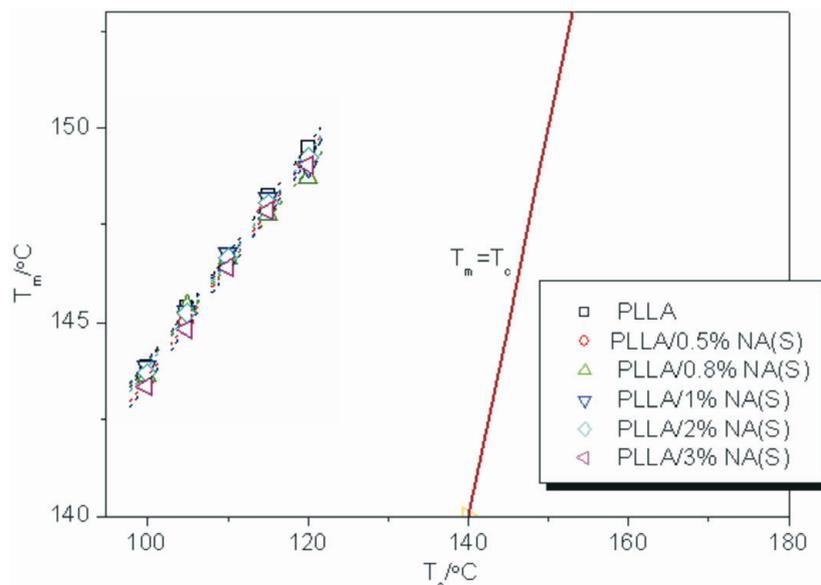


Figure 3 The equilibrium melting temperatures of pure PLLA and PLLA/NA samples.

Table 1 DSC data of PLLA/NA crystallized from melt at a cooling rate of  $1^{\circ}\text{min}^{-1}$ .

| Sample        | $T_c/^{\circ}\text{C}$ | $T_{m0}/^{\circ}\text{C}$ | $T_m/^{\circ}\text{C}$ | $\Delta H_c/\text{J g}^{-1}$ |
|---------------|------------------------|---------------------------|------------------------|------------------------------|
| PLLA          | 105.88                 | 96.28                     | 149.37                 | 1.379                        |
| PLLA/0.5 % NA | 117.27                 | 110.68                    | 146.31                 | 28.79                        |
| PLLA/0.8 % NA | 125.57                 | 118.24                    | 148.15                 | 31.63                        |
| PLLA/1 % NA   | 124.43                 | 117.39                    | 147.84                 | 31.10                        |
| PLLA/2 % NA   | 121.70                 | 116.29                    | 147.95                 | 29.94                        |
| PLLA/3 % NA   | 118.41                 | 112.63                    | 146.54                 | 29.75                        |

$T_m$ : melting temperature;  $T_{m0}$ : crystallization peak temperature.

Table 2 Equilibrium melting temperatures of pure PLLA and PLLA/NA samples.

| Sample        | $T_m^0/^{\circ}\text{C}$ | $\Delta T_m^0/^{\circ}\text{C}$ |
|---------------|--------------------------|---------------------------------|
| PLLA          | 161.2                    |                                 |
| PLLA/0.5 % NA | 161.1                    | 0.1                             |
| PLLA/0.8 % NA | 158.6                    | 2.6                             |
| PLLA/1 % NA   | 159.7                    | 1.5                             |
| PLLA/2 % NA   | 160.6                    | 0.6                             |
| PLLA/3 % NA   | 160.9                    | 0.3                             |

$$\Delta T_m^0/^{\circ}\text{C} = T_m^0/^{\circ}\text{C}(\text{PLLA}) - T_m^0/^{\circ}\text{C}(\text{PLLA/NA})$$

### 3.2. Equilibrium Melting

The equilibrium melting temperature of PLLA is higher than that of all PLLA/NA samples, which indicate that the crystallization of PLLA is more perfect, resulting from smaller spherulite size and increased nucleating density. These results further confirm that NA act as an effective heterogeneous nucleation agent. The equilibrium melting temperatures of pure PLLA and PLLA/NA samples were obtained using Hoffman-Weeks plots (see Fig. 3) and the results are listed in Table 2.

Compared with the equilibrium melting temperature of PLLA, PLLA/NA shows lower equilibrium melting temperatures and the equilibrium melting temperature strongly depends on the NA content. The equilibrium melting temperature of PLLA is higher than that of all PLLA/NA samples, which indicate that the crystallization of PLLA is more perfect, resulting from smaller spherulite size and increased nucleating density. These results further confirm that NA act as an effective heterogeneous nucleation agent.

### 3.3. Melting Behaviour

#### 3.3.1. PLLA/NA Melting Behaviour after Isothermal Crystallization

Figure 4 presents the melting endotherms of the PLLA/0.8%NA sample after the appearance of the whole exothermic peak during isothermal crystallization. Either single or double endotherms were observed at  $T_c$  temperatures ranging from 95 to 120  $^{\circ}\text{C}$ . The double-melting behaviour of PLLA has been reported in literature, and assigned to melting-recrystallization

by Yasuiwa<sup>10</sup>. The low-temperature melting peak is attributed to the primary crystallites formed at  $T_c$ , and the high-temperature melting peak reflect the relatively perfect lamella stacks resulting from recrystallization during the heating scan. At the same time, as seen in Fig. 4, a double-melting peak exists at low  $T_c$  and full crystallization time. This is due to a decrease in the macromolecule segment active ability and the crystallization of PLLA not being completed. The enhancement of the macro-

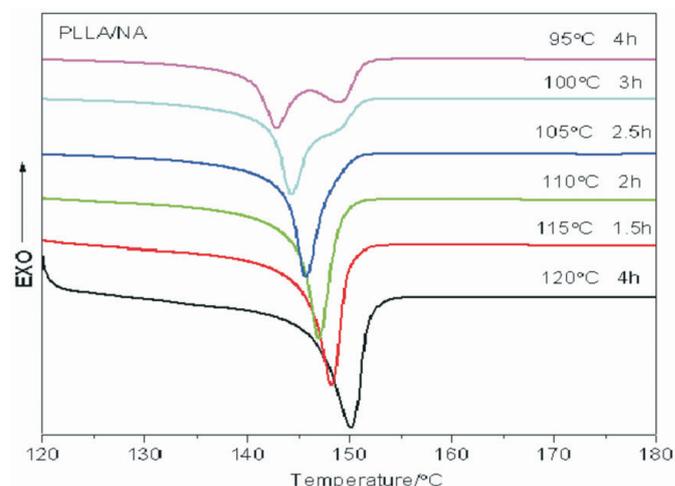
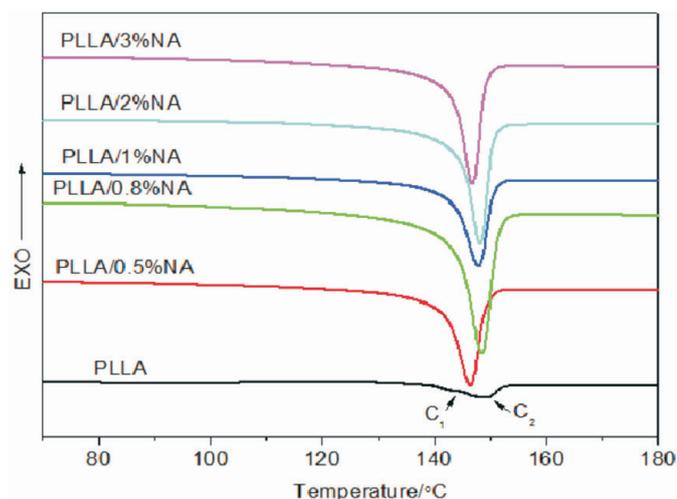


Figure 4 PLLA/NA melting behaviour after isothermal crystallization at different temperature.



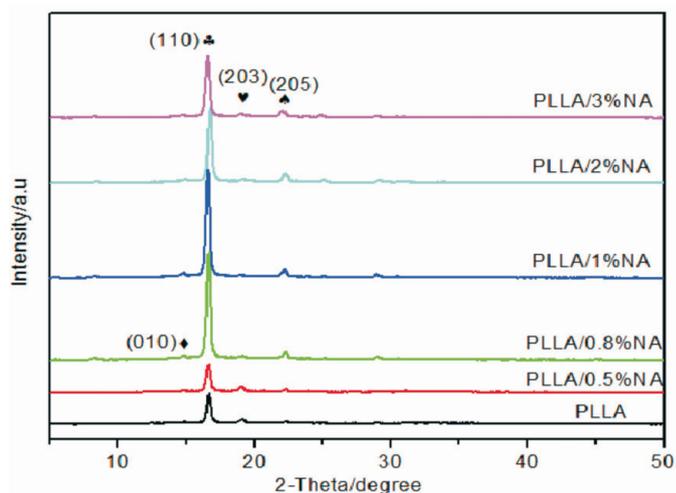
**Figure 5** PLLA/NA melting behaviour after non-isothermal crystallization.

molecule segment active ability improved the crystallization of PLLA resulting in increased crystallization temperature. On the other hand, the nucleating agent also increased the rate of crystallization of PLLA. The low-temperature melting peak gradually shifted to a higher temperature with increasing crystallization temperature. In contrast, the high-temperature melting peak shifted to a lower temperature. And the melting endotherms with double-melting peaks changed to a single endotherm. As seen in Fig. 4, the melting peak becomes much sharper at 105 to 115 °C, which indicates much more perfect crystallization of the PLLA. The low-temperature melting peak gradually shifted to a higher temperature with increasing crystallization temperature. In contrast, the high-temperature melting peak shifted to a lower temperature. And the melting endotherms with double melting peaks changed to a single endotherm. As seen in Fig. 4, the melting peak becomes much sharper at 105 to 115 °C, which indicates much more perfect crystallization of the PLLA.

### 3.3.2. PLLA/NA Melting Behaviour after Non-isothermal Crystallization

After non-isothermal crystallization from the melt at a cooling rate of 1 °C min<sup>-1</sup>, the melting behaviour of PLLA and PLLA/NA samples were investigated. Figure 5 presents the DSC curves recorded during the heating processes for heating scans of PLLA and PLLA/NA samples with different NA contents. In addition to the neat PLLA, all of the DSC curves show a single melting peak at higher temperature. This is due to PLLA/NA forming perfect crystals at a cooling rate of 1 °C min<sup>-1</sup>. The PLLA/NA samples melts directly without the melt recrystallization process. However, the crystallization of neat PLLA was very slow, PLLA undergoing a melt recrystallization-remelting process upon heating.

The effects of NA on the crystallization of PLLA were further investigated by WAXD. Figure 6 shows the WAXD of PLLA and PLLA/NA samples at a cooling rate of 1 °C min<sup>-1</sup>. The WAXD of the PLLA/NA samples are almost the same as those of the corresponding neat PLLA. The PLLA exhibits a very strongest reflection at  $2\theta = 16.6^\circ$  due to diffraction from (110) planes and other reflection peaks at  $2\theta = 19.2^\circ$  and  $2\theta = 22.3^\circ$  occurring from the (203) plane and (205) plane, respectively. With increasing NA content, the intensities of the strongest reflections (110) increases and a weak peak at  $14.8^\circ$ , assigned to the (010) diffraction plane,



**Figure 6** WAXD patterns of neat PLLA and PLLA/NA samples cooling from melt at 1 °C min<sup>-1</sup>.

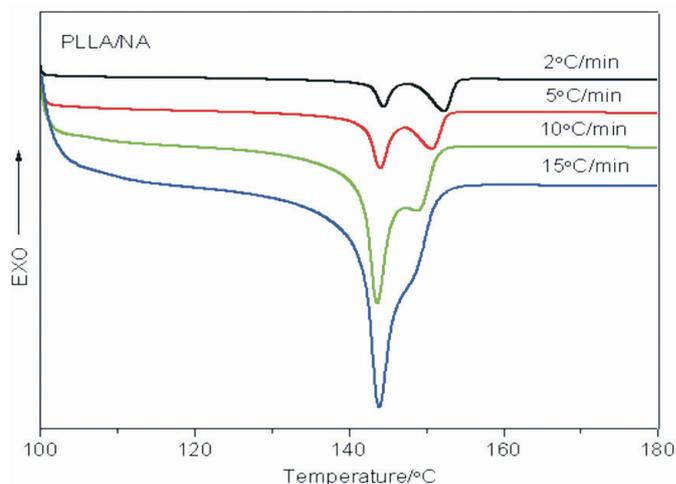
becomes evident. However, with the addition of more than 0.8 % NA, the intensities of the strongest reflections (110) becomes weaker.

### 3.3.3. PLLA/NA Sample Melting Behaviour at Different Heating Rates

The effects of NA on the melting behaviour of PLLA were further investigated by DSC. Figure 7 shows the isothermal crystallization of a PLLA/0.8%NA sample at different heating. With increasing heating rate, the double melting peak degenerates into a single melting peak and the high-temperature melting peak existed in the form of a pulse. From Fig. 7 it is clear that increasing heating rate leads to the shift of crystallization peak to higher temperature. On the other hand, the increasing heating rate made the degree of recrystallization of imperfect crystals decrease. This is further confirmation that the double melting peak results from melting-recrystallization.

## 3.4. Mechanical Properties

The tensile strengths, tensile modulus and elongation at break of PLLA with different NA content are presented in Fig. 8(a), Fig. 8(b) and Fig. 8(c), respectively. The figures show that NA can improve the tensile strength and modulus of PLLA, that the tensile strengths and tensile modulus increase with an increase in NA contents and possesses a maximum value for the critical



**Figure 7** PLLA/NA sample melting behaviour at different heating rate.

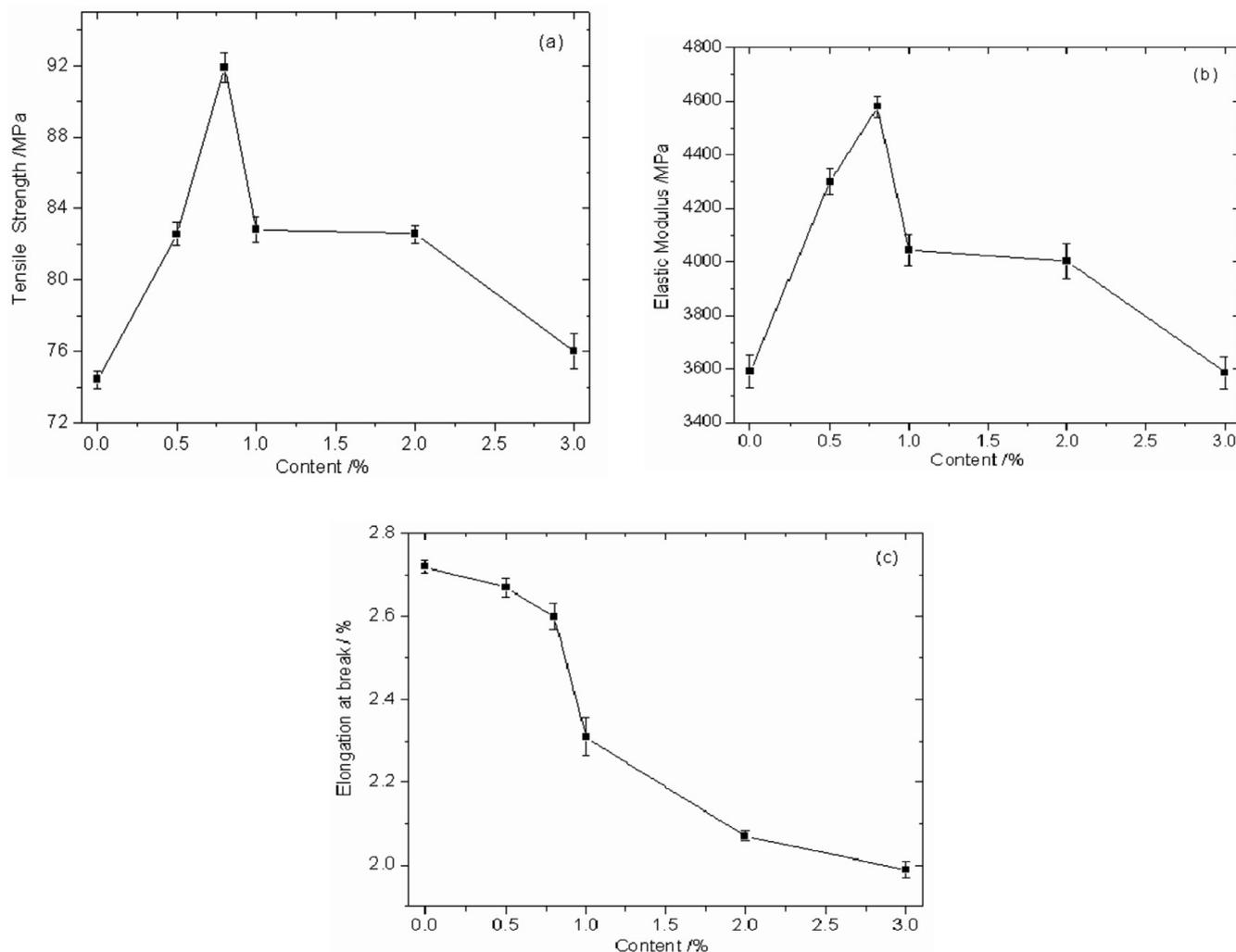


Figure 8 The mechanical properties of PLLA with different NA contents.

NA loading of 0.8 %. Upon addition of 0.8 % NA, comparing with the neat PLLA, the tensile strength and modulus increase from 74.4 MPa and 3592.8 MPa to 91.9 Mpa and 4580.9 Mpa, respectively. The enhancement of the tensile strength and modulus of PLLA/NA is due to the increase of degree of crystallization of PLLA with nucleating agent NA. When continuing to increase the NA content, the tensile strength and modulus started to decrease. The elongations at break of the samples are shown in Fig. 1(c). From this figure the effect of adding NA can be seen clearly and directly. NA can make PLLA become brittle. The reason is that NA makes the degree of crystallization of PLLA increase.

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