

Synthesis of *N, N'*-bis(benzoyl) azelaic acid dihydrazide and its Effect on Performance of Poly (L-lactic acid)

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Summary: In order to synthesize more function amides, *N, N'*-bis(benzoyl) azelaic acid dihydrazide (NA(A)) was synthesized from benzoyl hydrazine and azelaoyl chloride which was derived from azelaic acid via acylation. The influence of the reaction ratio, reaction time and reaction temperature to the yield of NA(A) was investigated by orthogonal experiment, the optimization result was: molar ratio of benzoyl hydrazine: azelaoyl chloride 2:3, reaction time 6 h, reaction temperature 70°C. The yield was 89.7%. Non-isothermal crystallization behavior measure indicated that NA(A) showed excellent nucleating effects on Poly(L-lactic acid) (PLLA) crystallization. Compared to the neat PLLA, with the addition of 0.8% NA(A), the crystallization temperature increased from 105.88°C to 122.99°C, the degree of supercooling decreased from 55.33°C to 36.96°C while the crystallization enthalpy increased from 1.379 J·g⁻¹ to 28.58 J·g⁻¹ at a cooling rate of 1°C/min from melt. The tensile strengths and tensile modulus increased with the increasing of NA(A) contents and possessed a maximum value for the critical NA(A) loading 0.3% and 0.5%, respectively. However, the elongations at break of PLLA/NA(A) samples decreased significantly. The hardness of PLLA/NA(A) samples after isothermal crystallization increased, and the largest value of hardness of PLLA/NA(A) with 1% NA(A) after isothermal crystallization was 176 N/mm².

Introduction

Amides have attracted more and more interests in recent years due to their antioxidative[1], highly active antiretroviral properties[2] and nucleating properties[3], etc. Especially, with the rapid development of science and technology, the amides and its derivatives have more and more range of applications such as synthetic intermediates[4], material chemistry[5], drug discovery[6], etc. For examples, Ajlouni *et al.*[7] reported a novel aryl amide and its complex were synthesized. The antioxidant activity of the aryl amide and its complexes was determined by DPPH radical scavenging method, which indicates that the complexes exhibit more effective antioxidant activity than the aryl amide alone. Li *et al.*[8] reported that the preliminary *in vivo* bioassays indicated novel fluorine-containing mandelic acid amide compounds showed excellent fungicidal activities *in vivo* against *Pseudoperonosporacubensis* at the dosage of 25 mg·L⁻¹, which were comparable with the control (Mandipropamid). Now, some researchers use amides as function additives of polymer to improve performance of polymer. Angela *et al.* [9] reported that ethylene bis-stearamide can serve as a nucleating agent of Poly (L-lactic acid) (PLLA) for dramatic increasing in crystallization rate and final crystalline content as indicated by isothermal and non-isothermal crystallization measurements. In our previous work[10-11], *N, N'*-bis(benzoyl) suberic

acid dihydrazide as heterogeneous nucleation agent can significantly improve the crystallization of PLLA. *N, N'*-bis(benzoyl) suberic acid dihydrazide leads to the shift of the melt crystallization to higher temperature and becomes much sharper in the melting crystallization process of PLLA. Upon the addition of 0.8% *N, N'*-bis(benzoyl) suberic acid dihydrazide, the crystallization half-time of PLLA/*N, N'*-bis(benzoyl) suberic acid dihydrazide decreases from 26.5 min to 1.4 min at 115°C.

N, N'-bis(benzoyl) suberic acid dihydrazide has been used to improve nucleating effect of PLLA, However, the effect on performance of PLLA is different due to different methyl of amide compound. Thus, in this paper, we synthesized the *N, N'*-bis(benzoyl) azelaic acid dihydrazide using an effective method, and its effect on performances including nucleating effect and mechanical properties of PLLA was also investigated.

Results and Discussion

Structure of NA (A)

The FT-IR spectra of NA(A) was shown in Fig. 1. In the spectra, the peaks at 3219.1cm⁻¹ contribute to the absorption of N-H stretching vibration and the plane bending vibration; the

absorption peaks at 2927.1cm^{-1} , 2854cm^{-1} and 706.1cm^{-1} contribute to CH_2 symmetrical stretching vibration, asymmetrical stretching vibration and rocking vibration respectively. The absorption peak at 3196.8cm^{-1} belongs to C-H stretching vibration of benzene, and the absorption peak at 1689cm^{-1} contribute to C=O stretching vibration of the amide group. Owing to conjugated effect between carbonyl and benzene, carbonyl absorption move to lower frequency. Thus, the absorption peak at 1647.7cm^{-1} contribute to C=O stretching vibration of benzoyl hydrazine. Then the absorption peaks at 1605.6cm^{-1} , 1574cm^{-1} , 1507cm^{-1} , 1468.5cm^{-1} proved the existence of benzene. The absorption peak at 1312.6cm^{-1} was mixed peak including C-N stretching vibration and N-H bending vibration absorption.

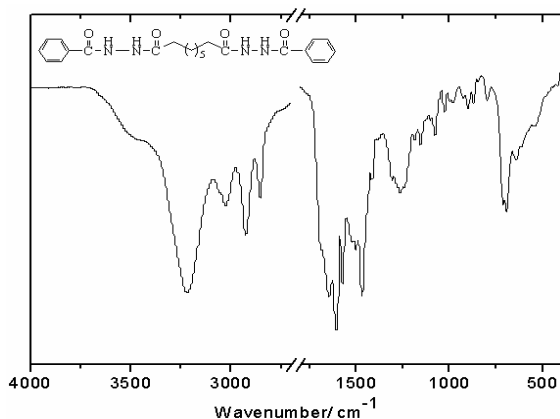


Fig. 1: IR spectra of NA(A).

The ^1H NMR patterns of NA(A) is depicted in Fig. 2. The single peak at $\delta_{\text{H}}=10.29$ and 9.84 are proton resonance peak of N-H of NA(A), the multiple peaks at $\delta_{\text{H}}=7.47$ - 7.88 are proton resonance peaks of benzene, the triplet peaks at $\delta_{\text{H}}=2.17$ - 2.20 are CH_2 which is near amide proton resonance peak, the multiple peaks at $\delta_{\text{H}}=1.32$ - 1.58 are other CH_2 proton resonance peaks.

Reaction Conditions of NA (A)

The influence of the reaction ratio, reaction time and reaction temperature to the yield of product was investigated by orthogonal experiment. Factors and level of orthogonal experiment are listed in Table-1, and the results are listed in Table-2. As seen in Table-2. It is clear that reaction temperature is more important to yield than other factors. And the optimized reaction condition is molar ratio of benzoyl hydrazine: azelaoyl chloride 2:3, reaction time 6h,

reaction temperature 70°C . However, the optimized reaction conditions are not listed in scheme of orthogonal experiment, thus, the optimized reaction condition need to be done to confirm the high yield of this reaction. The results showed that the highest yield is 89.7% under optimized reaction condition.

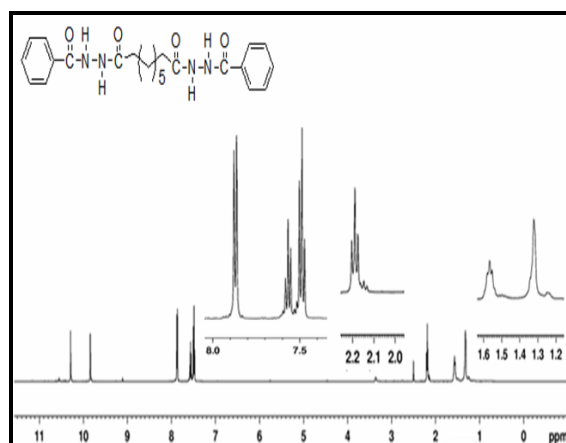


Fig. 2: ^1H NMR spectra of NA(A).

Table-1: Factors and level of orthogonal experiment.

Level	Factor		
	Reaction time (A)	Reaction ratio ^(a) (B)	Reaction temperature (C)
1	4h	1:1	60°C
2	6h	2:3	70°C
3	8h	1:2	80°C

(a) Benzoic hydrazide: azelaoyl chloride

Table-2: Orthogonal experiment result and analysis of NA(A).

Run	A	B	C	Scheme	Yield/%
1	1	1	1	A ₁ B ₁ C ₁	55.9%
2	1	2	2	A ₁ B ₂ C ₂	79.9%
3	1	3	3	A ₁ B ₃ C ₃	62%
4	2	2	3	A ₂ B ₂ C ₃	81.9%
5	2	3	1	A ₂ B ₃ C ₁	73.4%
6	2	1	2	A ₂ B ₁ C ₂	79.6%
7	3	3	2	A ₃ B ₃ C ₂	84.1%
8	3	1	3	A ₃ B ₁ C ₃	75.2%
9	3	2	1	A ₃ B ₂ C ₁	69.1%
K ₁	1.98	2.11	1.98		
K ₂	2.35	2.31	2.44		
K ₃	2.28	2.19	2.19		
k ₁	0.66	0.703	0.66		
k ₂	0.783	0.77	0.813		
k ₃	0.76	0.73	0.73		
Extreme difference	0.37	0.2	0.46		
Important factor	CAB				
Optimized scheme	A ₂ B ₂ C ₂				

Nucleating Effect of NA (A)

Fig. 3 shows the differential scanning calorimeter curve of non-isothermal crystallization

from melt at a cooling rate of 1°C/min. As seen in Fig. 3, upon cooling rate of 1°C/min, the crystallization peak of PLLA can hardly be detected, which shows that the crystallization of neat PLLA is very slow. With addition of NA(A), crystallization peak appears in the DSC cooling curve. Compared to the neat PLLA, NA(A) addition makes the crystallization peak appears and leads to the shift of crystallization peak to higher temperature indicating the increase of crystallization temperature while the crystallization peak for PLLA containing NA(A) becomes much sharper in the cooling process at the same time. These result indicates that NA(A) increased the overall crystallization rate of PLLA. Usually, degree of supercooling(ΔT_{mc}) could be expressed as the nucleating effect on crystallization. The smaller ΔT_{mc} is, the greater nucleating effect on PLLA crystallization is. As seen in Table-3, crystallization temperature(T_o) become higher with the increasing of NA(A) content, and the crystallization temperature(T_o) is the biggest upon the addition of 0.8% NA(A), which indicates that the best effect of crystallization is at 0.8% NA(A). Meantime, the ΔT_{mc} is the smallest, which also further confirmed the best effect of crystallization at 0.8% NA(A). Compared to the neat PLLA, with the addition of 0.8% NA(A), the crystallization temperature(T_o) increased from 105.88°C to 122.99°C and the crystallization enthalpy(ΔH_c) increased from 1.379 J·g⁻¹ to 28.58 J·g⁻¹. However, there existed the largest value of ΔH_c of PLLA/NA(A) sample with 3%NA(A).

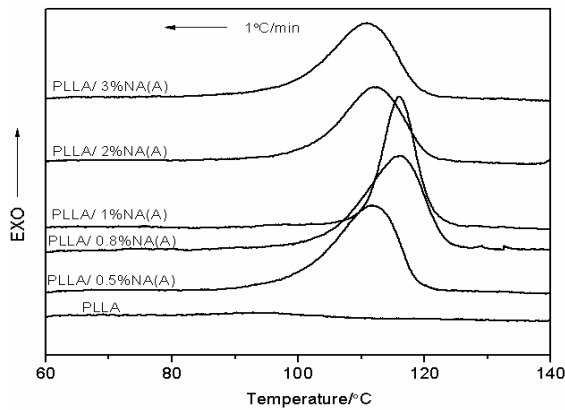


Fig. 3: DSC of PLLA and PLLA/NA(A) crystallized from melt at a cooling rate of 1°C/min.

Mechanical Properties of PLLA/NA(A)

The tensile strength, elastic modulus and elongations at break were obtained by averaging over

five specimens. The tensile strengths, tensile modulus and elongation at break of PLLA with different NA(A) contents are presented in Fig. 4(a-c), respectively. The Fig.4 shows that NA(A) can improve the tensile strength and tensile modulus of PLLA and decrease the elongations at break of PLLA. The tensile strengths and tensile modulus increased with the increase of NA(A) contents and had a maximum value for the critical NA(A) loading 0.3% and 0.5%, respectively. The value of tensile strength and tensile modulus of PLLA/NA(A) from 77.5 MPa and 3592.8 MPa to 80.8 MPa and 3959.6 MPa, respectively. The enhancement of the tensile strength and modulus of PLLA/NA(A) is due to the increasing of crystallization degree of PLLA with NA(A). The effect on of the elongations at break of PLLA is different that of tensile strength and modulus of PLLA/NA(A) sample.

Table-3: DSC data of PLLA/NA(A) crystallized from melt at cooling rate of 1°C/min.

Sample	T_o °C	T_{mc} °C	T_m °C	T_m^0 °C	ΔT_{mc} °C	ΔH_c J·g ⁻¹
PLLA	105.88	96.28	149.37	161.21	55.33	1.379
PLLA/0.5%NA(A)	118.91	111.64	146.73	161.07	42.16	31.88
PLLA/0.8%NA(A)	122.99	116.09	147.60	159.95	36.96	28.58
PLLA/1%NA(A)	120.83	116.14	147.55	160.19	39.36	30.66
PLLA/2%NA(A)	120.46	112.53	146.68	160.56	40.1	28.97
PLLA/3%NA(A)	119.20	110.76	146.38	161.13	41.93	31.11

T_m : melting temperature T_{mc} :crystallization peak temperature T_m^0 : equilibrium melting temperatures

Hardness of PLLA/NA(A)

The hardness of PLLA/NA(A) was measured using plastic ball indentation hardness tester. The measure result is listed in Table 4. As seen in Table 4, the hardness of PLLA/NA(A) samples after isothermal crystallization increase significantly, the possible reason is that the degree of crystallization increases after isothermal crystallization, which result in the increasing of hardness of PLLA/NA(A) samples. And the largest value of hardness of PLLA/ NA(A) with 1%NA(A) before/after isothermal crystallization are 149.6N/mm²/176N/mm².

Table-4: Hardness of PLLA/NA(A) sample.

Sample	Hardness(A)	Hardness(B)
PLLA/0.5%NA(A)	132.1N/mm ²	138.7N/mm ²
PLLA/0.8%NA(A)	144N/mm ²	173.2N/mm ²
PLLA/1%NA(A)	149.6N/mm ²	176N/mm ²
PLLA/2%NA(A)	145.1N/mm ²	170.5N/mm ²
PLLA/3%NA(A)	142.9N/mm ²	158.5N/mm ²

Hardness(A): Hardness before isothermal crystallization.

Hardness(B): Hardness after isothermal crystallization for 1h in 115°C.

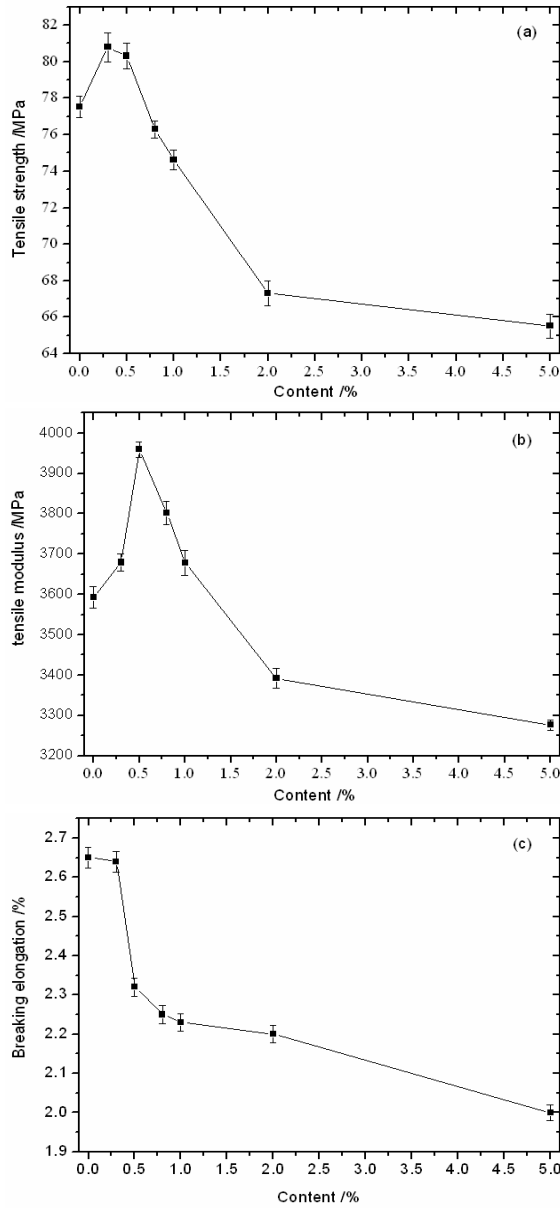


Fig. 4: The mechanical properties of PLLA with different NA(A) contents.

Experimental

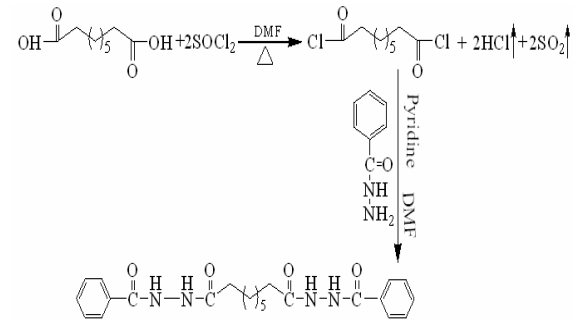
Materials

The materials used in this study were of analytical grade (AR) grade. Benzoyl hydrazine and azelaic acid were procured from Chengdu Kelong Chemical Reagents Company respectively (Sichuan Province, China); thionyl chloride, *N,N*-dimethylacetamide and pyridine were procured from

Mianyang Rongshen Chemical Reagents Company (Sichuan Province, China). Poly(L-lactic acid) (2002D) was purchased from Nature Works LLC, USA.

Synthesis of *N,N'*-bis (benzoyl) azelaic acid dihydrazide (NA(A))

NA(A) was prepared as shown in Scheme-1. And the specific reaction process have described in our previous paper [10].



Scheme-1: Synthesis of *N,N'*-bis(benzoyl) azelaic acid dihydrazide.

Preparation of PLLA/NA(A) Samples

PLLA was dried overnight at 50°C under vacuum to remove residual water. Blending of PLLA and dried NA (A) was performed on a counter-rotating mixer with a rotation speed of 32 rpm for 5min, then at 64 rpm for 5 min. The processing temperature was set at 185°C. PLLA/NA(A) samples 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 down to room temperature by being compressed at room temperature under 20 MPa for 10 min.

Test

Fourier transform infrared spectra were recorded on a Bio-Rad FTS135 spectrophotometer from 4000 to 400 cm⁻¹. The sample of NA(A) was mixed with KBr powders and pressed into a disk suitable for IR measurement.

The ¹H nuclear magnetic resonance of NA(A) was recorded on Bruker AVANCE 300 spectrometers. The solvent was dimethyl sulfoxide (DMSO).

The non-isothermal crystallization behavior of PLLA/NA(A) was measured by DSC Q2000. 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 melted completely. Then the samples were cooled from the melt state to 40°C at a cooling rate of 1°C/min.

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 at room temperature. The tensile strength, elastic modulus and elongations at break were obtained by averaging over five specimens.

Conclusions

In this paper, *N, N'*-bis(benzoyl) azelaic acid dihydrazide(NA(A)) was synthesized. And we investigated influence of the molar ratio, reaction temperature and reaction time to the yields of product by orthogonal experiment. Non-isothermal crystallization behavior measure indicated that NA(A) showed excellent nucleating effects on PLLA crystallization. The mechanical properties including tensile strengths, tensile modulus and the elongations at break of PLLA/NA(A) samples were investigated in detail. The hardness of PLLA/NA(A) samples after isothermal crystallization increased significantly.

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