

The effect of *N,N'*-bis(benzoyl)dodecanedihydrazide on enhancing the crystallization rate of poly(L-lactic acid)

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Abstract: The effect of *N,N'*-bis(benzoyl)dodecanedihydrazide (BADH) as a newly-developed organic nucleating agent on the crystallization process of poly(L-lactic acid) (PLLA) was examined in this study. Non-isothermal crystallization results indicated that BADH had excellent acceleration effects on the melt-crystallization of PLLA, and a larger proportion of BADH promoted more powerful crystallization. However, BADH inhibited the crystal growth of PLLA during the cold-crystallization process, and an increase of BADH concentration caused the non-isothermal crystallization peak to shift towards a higher temperature and become much wider. Although increased cooling rates might decrease nuclei density, it was surprising to see that BADH contents of 2 wt % to 3 wt % were able to accelerate the crystallization of PLLA upon fast cooling at 20 °C/min or even higher cooling rates. Besides, the effect of the final melting temperature on the melt-crystallization process of PLLA was not negligible, the relevant results implied that 190 °C was the optimal blending temperature of PLLA and BADH. Isothermal crystallization showed that, in the best case of the PLLA/3% BADH sample, the half-time of crystallization has a minimum value of 22.9 s at 115 °C. The calculation of frontier molecular orbital energies confirmed that the interaction between PLLA and BADH could form more easily during the melting blend than PLLA itself, indicating that the probable nucleating mechanism was chemical nucleation.

Keywords: poly(L-lactic acid), nucleation effect, crystallization behavior, dodecanedioic dihydrazide, nucleating mechanism.

Szybkość krystalizacji poli(kwasu L-mlekowego) inicjowanej *N,N'*-bis(benzoilo)dodekanodihydrazidem

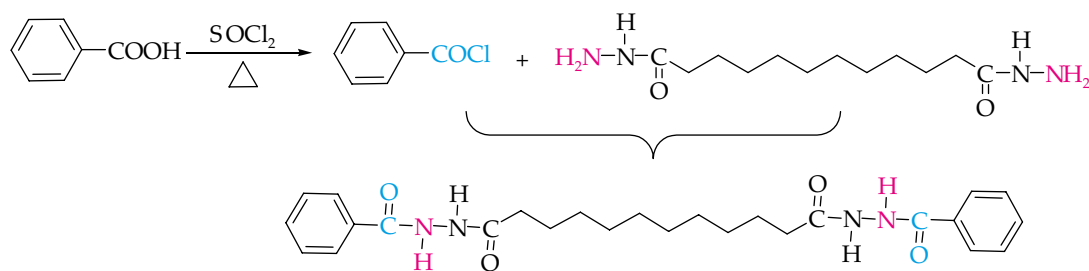
Streszczenie: Oceniano wpływ nowo opracowanego organicznego środka zarodkującego – *N,N'*-bis(benzoilo)dodekanodihydrazidu (BADH) – na krystalizację poli(kwasu L-mlekowego) (PLLA). Wyniki badania nieizotermicznej krystalizacji PLLA wskazują, że dodatek BADH silnie przyspiesza krystalizację w stopie, a zwiększenie ilości BADH w stopionym PLLA skutkuje jego efektywniejszą krystalizacją. Dodatek BADH w takim samym stężeniu opóźnia jednak zimną krystalizację PLLA, pik temperatury krystalizacji poszerza się i przesuwa w kierunku większych wartości temperatury. Choć zwiększenie szybkości chłodzenia może zmniejszać gęstość zarodkowania, to dodatek 2–3 % mas. BADH do PLLA w tych warunkach zwiększa szybkość krystalizacji, przy szybkości chłodzenia nawet do 20 °C/min. Wpływ końcowej temperatury topnienia stopu na szybkość krystalizacji był istotny; stwierdzono, że optymalną temperaturą topnienia PLLA z BADH jest 190 °C. Badania kinetyki izotermicznej krystalizacji wykazały, że próbka PLLA/3% BADH charakteryzuje się najmniejszą wartością $t_{1/2}$ w temperaturze 115 °C. Obliczenia w programie DMol³ granicznej molekularnej energii orbitalnej potwierdziły, że podczas topienia mieszanki PLLA i BADH łatwiej dochodzi do interakcji niż podczas topienia czystego PLLA, co wskazuje, że prawdopodobnym mechanizmem zarodkowania jest zarodkowanie chemiczne.

Słowa kluczowe: poli(kwas mlekowy), efekt zarodkowania, przebieg krystalizacji, dihydrazyd dodekanodiowy, mechanizm zarodkowania.

Poly(L-lactic acid) (PLLA) is the most promising, environment-friendly polyester for commercial applications, and many research works have been performed to explore its distinct role in fields such as biomedicine [1, 2], packag-

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Scheme A

ing [3, 4], electronics [5], automobiles [6], *etc.* However, extremely slow crystallization rates leads to poor heat resistance and unstable mechanical properties resulting from no obvious crystallization [7]. The addition of a nucleating agent is one of the most effective ways to improve the crystallization of PLLA [8] because a nucleating agent can reduce the surface free energy barrier toward nucleation and so promote crystallization. Up to now, many nucleating agents – including inorganic nucleating agents and organic nucleating agents – were chosen or prepared to evaluate their crystallization promoting effects on PLLA. For inorganic nucleating agents, many inorganic nucleating agents, including talc [9], montmorillonite [10], zinc citrate [11], MOFs (metal-organic frameworks) [12], exhibit very powerful nucleation efficiencies but inorganic nucleating agents often need chemical modifications to enhance their compatibility with PLLA before use, which increases the price of large-scale PLLA production. What is worse, the chemical modification may weaken the nucleation ability of inorganic nucleating agents for PLLA [13]. Therefore, organic nucleating agents have attracted more attention, and myo-inositol [14], salicyloyl hydrazide derivative [15], tetramethylenedicarboxylic dibenzoylhydrazide [16], *N,N'*-bis(benzoyl)adipic acid dihydrazide [9], cyanuric acid [17] were chosen or synthesized as crystallization promoters for PLLA. Unfortunately, the ability of most organic nucleating agents to accelerate crystallization is slightly poorer than that of inorganic nucleating agents. Thus, developing efficient organic nucleating agents is very necessary to overcome the slow crystallization rate of PLLA and the defects of inorganic nucleating agents.

In this report, an organic compound, *N,N'*-bis(benzoyl)-dodecanedioic dihydrazide (designated here as BADH), was synthesized *via* acylation and amination reactions, and the influence of BADH on the crystallization process of PLLA was investigated through a series of comparative studies.

EXPERIMENTAL PART

Materials

2002D PLLA with $1.95 \cdot 10^5 M_w$ and 4.25 % of D-isomer content was purchased from Nature Works LLC, USA.

All reagents, including benzoic acid, *N,N'*-dimethylformamide (DMF), thionyl chloride, dodecane-

dioic dihydrazide and triethylamine, were obtained from Chongqing Huanwei Chemical Co., Ltd. China.

Synthesis and characterization of BADH

The synthesis route of BADH is shown in Scheme A. Firstly, benzoyl chloride was synthesized using an acylation reaction according to previous, similar experimental operations [18, 19]. Secondly, dodecanedioic dihydrazide was dissolved in DMF, and then adding the benzoyl chloride into the mixed solution in an ice bath with continuous stirring for 1 h, afterwards, the mixture was heated to 40 °C for 4 h with stirring to form a white, turbid solution. Finally, the white, turbid solution was filtered and washed with water 3 times and dried overnight at 45 °C under a vacuum. The molecular structure of BADH was determined using a Bruker AVANCE III HD 400M nuclear magnetic resonance spectrometer (the solvent: deuterated dimethyl sulfoxide) and IS50 infrared spectrometer (KBr pellet technique).

IR (KBr) ν cm^{-1} : 3316.7, 3290.2, 3044.6, 2921.9, 2848.7, 1693.7, 1632.7, 1580.9, 1536.8, 1488.7, 1472.4, 1461.3, 1380.2, 1328.8, 1290.7, 1270.6, 1245.7, 1223.1, 1161.6, 1107.9, 1040.3, 1012.2, 973.9, 952.9, 901.4, 731.6, 692.9, 619.7;

^1H NMR (DMSO- d_6 , 400 MHz) δ ppm: 10.27 (s, 1H, NH), 9.82 (s, 1H, NH), 7.47–7.88 (m, 5H, Ar), 2.73–2.77 (d, 2H, CH_2), 1.97–2.20 (m, 2H, CH_2), 1.48–1.55 (t, 4H, CH_2), 1.22–1.29 (t, 2H, CH_2).

Preparation of PLLA/BADH samples

The preparation of PLLA containing different BADH concentrations was performed using melting blend technology, and the processing parameters were: blending temperature 190 °C, mixing at 32 rpm for 10 min, and 64 rpm for 7 min. Afterwards, the blending mixtures were heat pressed and cool pressed to prepare sheets with a thickness of 0.4 mm for crystallization studies.

Methods of testing

The non-isothermal crystallization behavior of the pristine PLLA and PLLA/BADH was evaluated using a TA Q2000 differential scanning calorimeter (DSC), and GJY-III optical depolarizer to determine the isothermal

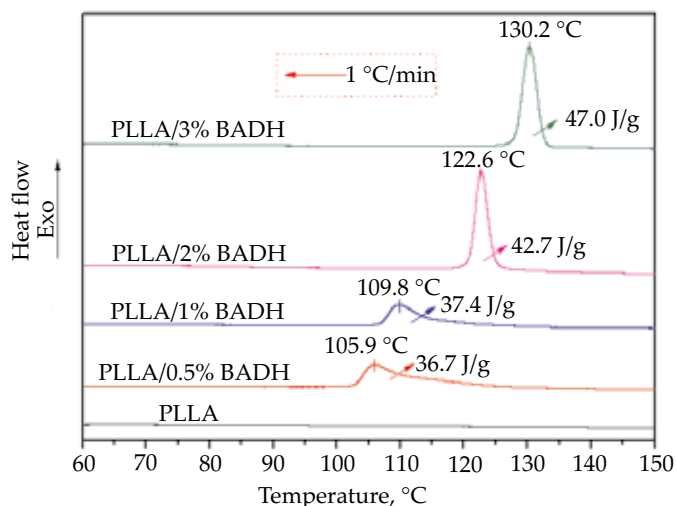


Fig. 1. Non-isothermal crystallization of pristine PLLA and PLLA/BADH samples at a cooling rate of 1 °C/min

crystallization behavior in the temperature region from 100 °C to 125 °C.

RESULTS AND DISCUSSION

Non-isothermal crystallization

Investigation of the non-isothermal crystallization behavior of polymers is very instructive to industrial production. Figure 1 shows the DSC curves of non-isothermal crystallization of the pristine PLLA and PLLA/BADH samples from 190 °C at a cooling rate of 1 °C/min. As seen in Fig. 1, there is almost no non-isothermal crystallization peak upon cooling for the pristine PLLA indicating that the crystallization ability of the primary PLLA itself is very poor. In contrast with the pristine PLLA, the addition of BADH results in the PLLA matrix having quite different DSC curves. That is, all PLLA/BADH samples exhibit obvious non-isothermal crystallization peaks with different locations and heights, which shows that the BADH, as a heterogeneous nucleating agent, plays an

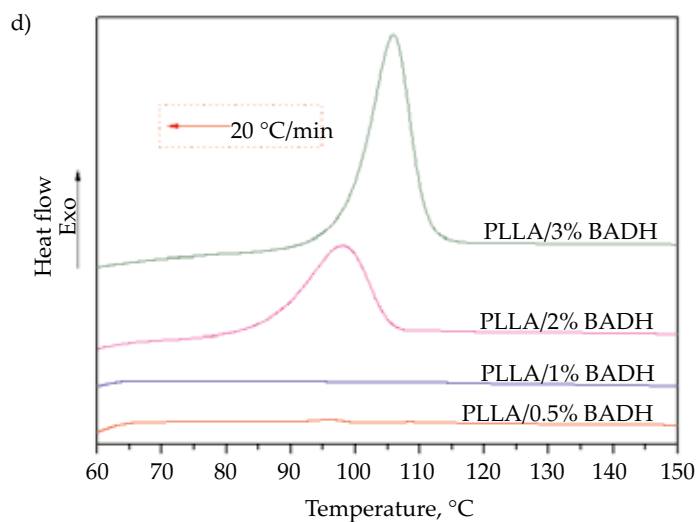
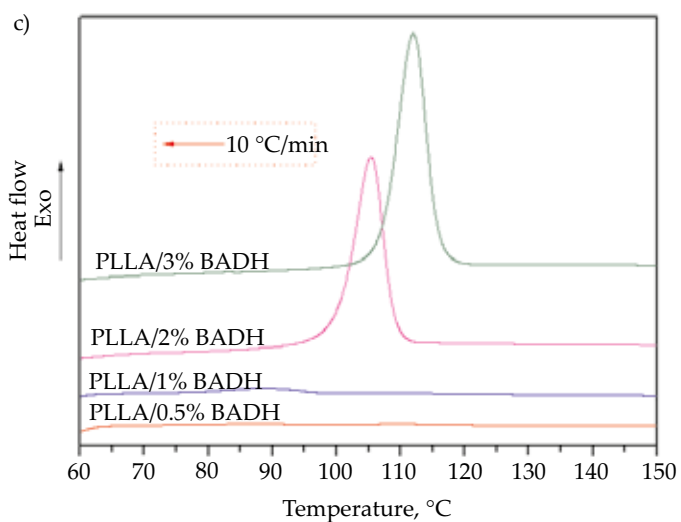
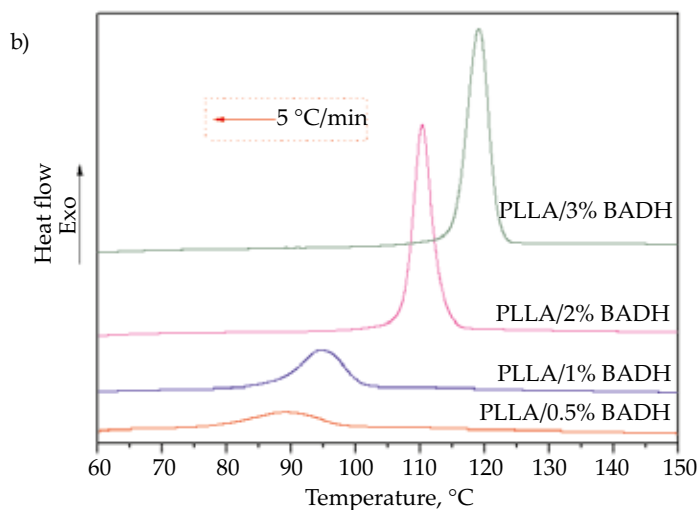
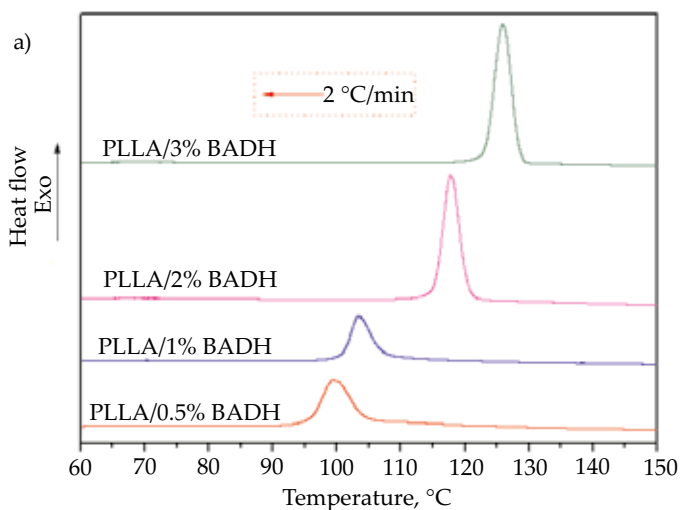


Fig. 2. Non-isothermal crystallization of pristine PLLA and PLLA/BADH samples at different cooling rates: a) 2 °C/min, b) 5 °C/min, c) 10 °C/min, d) 20 °C/min

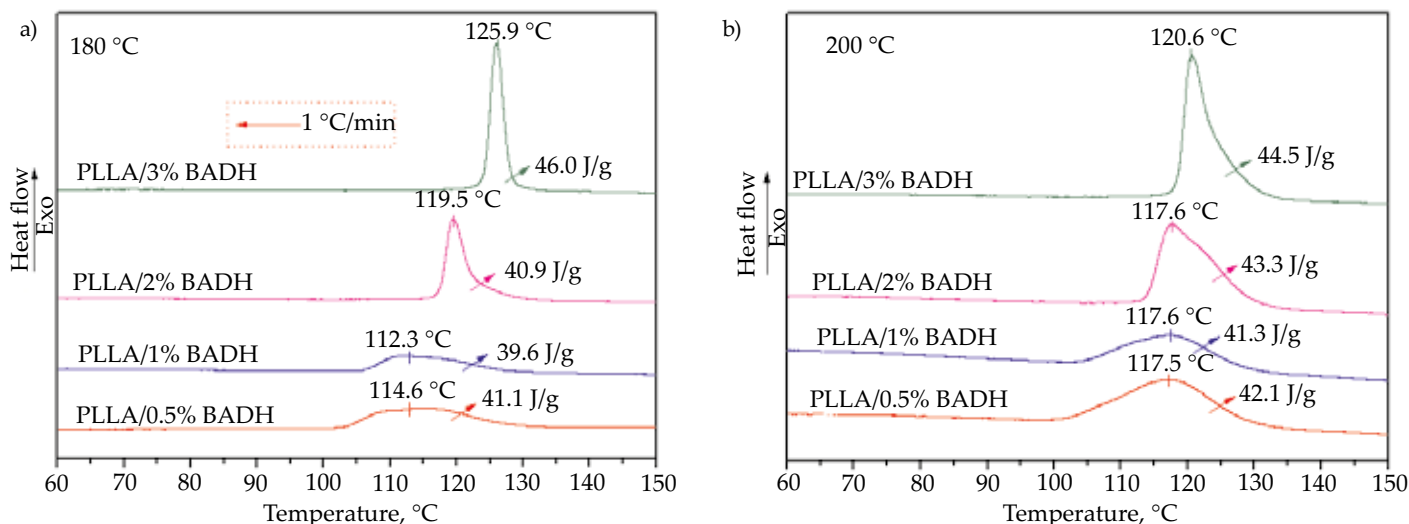


Fig. 3. DSC curves of PLLA/BADH samples from different final melting temperatures: a) 180 °C, b) 200 °C, at a cooling rate of 1 °C/min

important catalytic role in the crystallization of PLLA. Additionally, the non-isothermal crystallization peak shifts toward a higher temperature and becomes much sharper with higher BADH concentrations, as well as the larger non-isothermal crystallization enthalpy, revealing the best nucleating efficiency of 3 wt % BADH. Upon the addition of 3 wt % BADH, the crystallization peak temperature and crystallinity of PLLA can rise to 130.2 °C and 51.7 % (the melting enthalpy of 100 % crystalline PLLA is 93.7 J/g [20]).

Although an increased cooling rate must decrease the nuclei density in the polymer matrix [21], it is very helpful to investigate the effect of higher cooling rates on the crystallization behavior to meet industrial production requirements. Figure 2 shows the non-isothermal crystallization process of BADH-nucleated PLLA at different cooling rates. It is found that, with increased cooling rates, all non-isothermal crystallization peaks become wider and shift to lower temperatures, suggesting that a higher cooling rate greatly weakens the accelerating effect of BADH on crystallization. Particularly when the cooling rate is 10 °C/min, PLLA/0.5% BADH and PLLA/1% BADH almost have no crystallization peaks upon cooling. However, PLLA/2% BADH and PLLA/3% BADH still exhibit visible and sharp crystallization peaks upon cooling at 20 °C/min, indicating that a moderate amount of BADH (from 2 wt % to 3 wt %) is able to accelerate the crystallization of PLLA upon fast cooling at 20 °C/min and even higher cooling rates, which is beneficial for PLLA production that requires rapid crystallization during manufacturing.

To explore the optimized processing temperature, the influence of the final melting temperature on the crystallization of PLLA was further investigated (Fig. 3). As seen in Fig. 3, the final melting temperature significantly affects the crystallization process of PLLA, and this effect can be divided into two types depending on the final melting temperature. When the BADH concentration is 0.5 wt % to 1 wt %, for a given PLLA/BADH sample, both the crystallization peak temperature and non-isothermal

crystallization enthalpy share a similar tendency, that is, the crystallization peak temperature and non-isothermal crystallization enthalpy firstly decrease, and then increase with higher final melting temperatures (see Figs. 1 and 3). Moreover, the PLLA/0.5% BADH sample, in comparison to other PLLA/BADH samples, has the largest difference in crystallization peak temperature and non-isothermal crystallization enthalpy as a function of different final melting temperatures, and the differences are 11.6 °C and 5.4 J/g, respectively (Figs. 1 and 3). In contrast, upon the addition of 2 wt % to 3 wt % BADH, the crystallization peak temperature and non-isothermal crystallization enthalpy of a given PLLA/BADH sample firstly increase, then decrease with higher final melting temperatures. To conclude, according to our results, as well as the aforementioned effect of BADH concentration on the crystallization of PLLA, 190 °C is the optimized blending temperature.

The aforementioned DSC results of the melt crystallization provided evidence that BADH is a nucleating agent for PLLA and improves the crystallization performance.

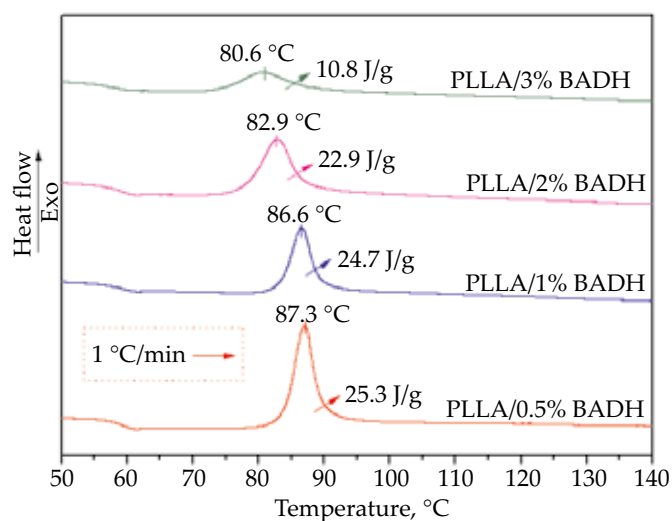


Fig. 4. DSC curves of PLLA/BADH from 50 °C at a heating rate of 1 °C/min

On the other hand, it is also necessary to estimate the role of BADH in the PLLA matrix during heating. Figure 4 shows the DSC curves of PLLA/BADH samples from 50 °C at a heating rate of 1 °C/min, where it was observed that the crystallization peak shifts to lower temperatures and becomes wider, as well as the crystallization enthalpy decreases, at higher BADH concentrations, exhibiting a thorough adverse result from melt crystallization. During heating, PLLA itself and BADH can form a very high nucleation density in the PLLA matrix, so the crystal growth rate is the rate-determining step. Meantime, it is because of the powerful nucleation effect of BADH that a slightly excessive BADH concentration inhibits crystal growth. That is, the higher the BADH concentration in the PLLA matrix, the stronger the impediment effect is, resulting in the aforementioned testing results.

Isothermal crystallization

Investigation of the isothermal crystallization behavior can give the half-time of crystallization ($t_{1/2}$), which is a crucial parameter to evaluate the overall crystallization rate of PLLA modified with BADH. The $t_{1/2}$ for the pristine PLLA and PLLA/BADH samples with different BADH contents plotted as a function of crystallization temperature is shown in Fig. 5. For the pristine PLLA, the $t_{1/2}$ does not exhibit a regular change with higher crystallization temperatures because the crystallization process depends on the nuclear rate and crystal growth rate. In the low-temperature region, the pristine PLLA has a faster nuclear rate than crystal growth rate; in contrast, the crystal growth rate is faster than the nuclear rate in the high-temperature region. This competitive relationship results in a minimum $t_{1/2}$ value for pristine PLLA of 139.2 s at 120 °C. For the BADH-nucleated PLLA, an increase of BADH concentration can cause the $t_{1/2}$ to decrease significantly at a given crystallization temperature, indicating that PLLA/3% BADH has the fastest crystallization rate, which is consistent with the aforementioned non-isothermal crystallization results. However, the minimum $t_{1/2}$ values of all PLLA/BADH samples do not appear at same crystallization temperature, and when the BADH concentration is 0.5 wt % to 1 wt %, the minimum $t_{1/2}$ values of PLLA/BADH samples occur at 105 °C; whereas when the BADH concentration is 2 wt % to 3 wt %, the minimum $t_{1/2}$ values of PLLA/BADH samples appear at the higher crystallization temperature of 115 °C, and PLLA/3% BADH has a minimum $t_{1/2}$ value of 22.9 s at 115 °C, which means that PLLA products only need less than 1 min to crystallize completely during manufacturing, what is more is that this crystallization temperature is higher than the commonly reported optimal temperature range 100–110 °C [7, 22, 23], and the $t_{1/2}$ is shorter at the same crystallization temperature compared to other systems such as PLLA/TFC (twice-functionalized organoclay) [20], PLLA/talc [24], PLLA/*N,N'*-bis(benzoyl)sebacic acid dihydrazide [25], PLLA/BSAD [*N,N'*-bis(benzoyl)sebacic acid dihydrazide] [26].

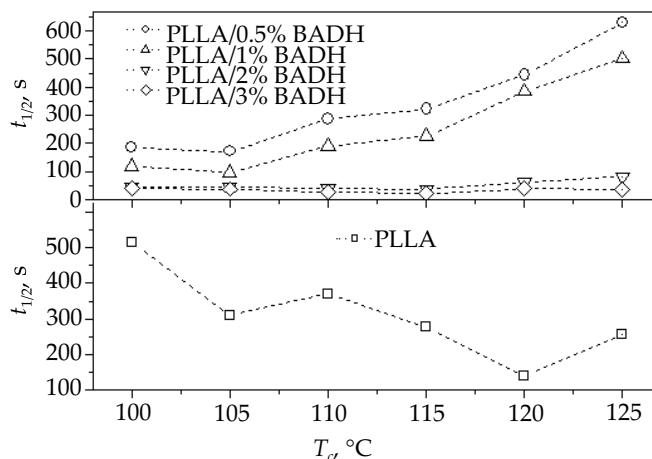


Fig. 5. Effect of BADH content and crystallization temperature against the $t_{1/2}$

Proposed nucleating mechanism

For the interaction mechanism of a nucleating agent, there are two nucleation mechanisms to consider – chemical nucleation and epitaxial nucleation [27]. According to molecular structure analysis, chemical nucleation is expected to occur between BADH and PLLA through a probable interaction between the C=O of PLLA and N-H of BADH. As a first step to confirm this hypothesis, a theoretical calculation of geometry optimization was performed using the modeling program DMol³. The optimal geometry structures of PLLA with ten repeating units and BADH were obtained (Fig. 6), and the calculation results show that the HOMO and LUMO are, respectively, -11.082 eV and 0.251 eV for PLLA, and -0.203 eV and -0.081 eV for BADH. Frontier molecular orbital theory suggests that the reactivity model is based upon the LUMO-HOMO energy gap ΔE , the smaller the ΔE is, the more easily the interaction is formed. The ΔE of 11.001 eV between PLLA and BADH is smaller than that of 11.333 eV for PLLA itself, which illustrates that the interaction between PLLA and BADH can form more easily when melting the blend. More in-depth experiments certainly need to be performed to verify this nucleation mechanism in the lab.

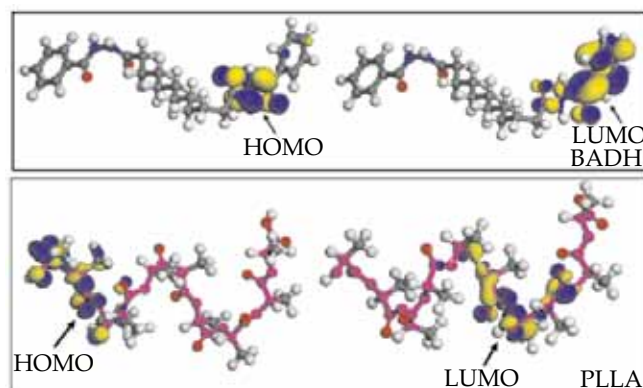


Fig. 6. The optimal geometry structures of PLLA and BADH

CONCLUSIONS

A novel organic nucleating agent, BADH, was synthesized through acylation and amination, and the nucleating effect of BADH for PLLA was studied by DSC and optical depolarization. The non-isothermal crystallization behavior showed that BADH could significantly accelerate the melt-crystallization of PLLA. Upon the addition of 3 wt % BADH, the crystallization peak temperature and crystallinity of PLLA rose to 130.2 °C and 51.7 % compared to the unobserved crystallization peak for the pristine PLLA. Additionally, both the cooling rate and the final melting temperature significantly affected the melt-crystallization process. However, the effect of BADH concentration on the cold-crystallization process was an opposite result from that of the melt-crystallization process. Isothermal crystallization results further confirmed that the addition of BADH could enhance the crystallization rate of PLLA, and PLLA/3% BADH had a minimum $t_{1/2}$ of 22.9 s at 115 °C. According to the frontier molecular orbital energy calculation and molecular structure analysis of PLLA and BADH, chemical nucleation was proposed.

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REFERENCES

- [1] Moroi A., Okuno M., Kobayashi G. *et al.*: *Journal of Biomedical Materials Research Part B: Applied Biomaterials* **2018**, 106 (1), 191.
<https://doi.org/10.1002/jbm.b.33833>
- [2] Yan Y., Sencadas V., Jin T.T. *et al.*: *Journal of Colloid and Interface Science* **2017**, 508, 87.
<https://doi.org/10.1016/j.jcis.2017.08.033>
- [3] Wang L., Lee R.E., Wang G.L. *et al.*: *Chemical Engineering Journal* **2017**, 327, 1151.
<https://doi.org/10.1016/j.cej.2017.07.024>
- [4] Genovese L., Soccio M., Lotti N. *et al.*: *European Polymer Journal* **2017**, 95, 289.
<https://doi.org/10.1016/j.eurpolymj.2017.08.001>
- [5] Wang Y.H., Shi Y.Y., Dai J. *et al.*: *Polymer International* **2013**, 62 (6), 957.
<https://doi.org/10.1002/pi.4383>
- [6] Wang Y.H., Xu X.L., Dai J. *et al.*: *RSC Advances* **2014**, 103 (4), 59 194.
<http://dx.doi.org/10.1039/C4RA11282B>
- [7] Feng Y.Q., Ma P.M., Xu P.W. *et al.*: *International Journal of Biological Macromolecules* **2018**, 106, 955.
<https://doi.org/10.1016/j.ijbiomac.2017.08.095>
- [8] Fan Y.Q., Zhu J., Yan S.F. *et al.*: *Polymer* **2015**, 67, 63.
<https://doi.org/10.1016/j.polymer.2015.04.062>
- [9] Xue B., Guo D., Bao J.J.: *Journal of Polymer Engineering* **2016**, 36 (4), 381.
- [10] Wu T., Tong Y.R., Qiu F. *et al.*: *Polymers for Advanced Technologies* **2018**, 29, 41.
<https://doi.org/10.1002/pat.4087>
- [11] Teranishi S., Kusumi R., Kimura F. *et al.*: *Chemistry Letters* **2017**, 46 (6), 830.
- [12] Shi X.W., Dai X., Cao Y. *et al.*: *Industrial & Engineering Chemistry Research* **2017**, 56 (14), 3887.
<http://dx.doi.org/10.1021/acs.iecr.6b04204>
- [13] Liang Y.Y., Xu J.Z., Liu X.Y. *et al.*: *Polymer* **2013**, 54 (23), 6479. <https://doi.org/10.1016/j.polymer.2013.09.027>
- [14] Shi H., Chen X., Chen W.K. *et al.*: *Journal of Applied Polymer Science* **2017**, 134 (16), 44 732.
<https://doi.org/10.1002/app.44732>
- [15] Cai Y.H., Tian L.L., Tang Y.: *Polimery* **2017**, 62, 734.
<http://dx.doi.org/10.14314/polimery.2017.734>
- [16] Cui L., Wang Y.H., Guo Y. *et al.*: *Polymers for Advanced Technologies* **2016**, 27 (10), 1301.
<https://doi.org/10.1002/pat.3795>
- [17] Weng M.T., Qiu Z.B.: *Thermochimica Acta* **2014**, 577, 41.
<https://doi.org/10.1016/j.tca.2013.12.011>
- [18] Cai Y.H., Zhao L.S.: *E-Polymers* **2016**, 16 (4), 303.
<https://doi.org/10.1515/epoly-2016-0052>
- [19] Cai Y.H., Zhao L.S., Tian L.L.: *Polymer Bulletin* **2017**, 74 (9), 3751.
<https://doi.org/10.1007/s00289-017-1923-4>
- [20] Li X.X., Yin J.B., Yu Z.Y. *et al.*: *Polymer Composites* **2009**, 30, 1338.
<https://doi.org/10.1002/pc.20721>
- [21] Jalali A., Huneault M.A., Elkoun S.: *Journal of Materials Science* **2016**, 51 (16), 7768.
<https://doi.org/10.1007/s10853-016-0059-5>
- [22] Saeidlou S., Huneault M.A., Li H., Park C.B.: *Progress in Polymer Science* **2012**, 37, 1657.
<https://doi.org/10.1016/j.progpolymsci.2012.07.005>
- [23] Liu G., Zhang X., Wang D.: *Advanced Materials* **2014**, 26, 6905.
<https://doi.org/10.1002/adma.201305413>
- [24] Xiao H.Q., Guo D., Bao J.J.: *Journal of Applied Polymer Science* **2015**, 132 (7), 41 454.
<https://doi.org/10.1002/app.41454>
- [25] Cai Y.H., Yan S.F., Yin J.B. *et al.*: *Journal of Applied Polymer Science* **2011**, 121 (3), 1408.
<https://doi.org/10.1002/app.33633>
- [26] Fan Y.Q., Yu Z.Y., Cai Y.H. *et al.*: *Polymer International* **2013**, 62 (4), 647.
<https://doi.org/10.1002/pi.4342>
- [27] Pan P.P., Liang Z.C., Cao A., Inoue Y.: *ACS Applied Materials & Interfaces* **2009**, 1 (2), 402.
<http://dx.doi.org/10.1021/am800106f>