Crystallization and melting behavior of poly(L-lactic acid) modified with salicyloyl hydrazide derivative

Yan-Hua Cai[1), *)], **Liang-Liang Tian**[1), *)], **Ying Tang**[1)]

DOI: dx.doi.org/10.14314/polimery.2017.734

Abstract: This work evaluated the influence of a novel organic nucleating agent, salicyloyl hydrazide derivative (BS), on the crystallization and melting behavior of poly(L-lactic acid) (PLLA). Differential scanning calorimetry revealed that the incorporation of BS (0.2 to 3 wt %) significantly promoted the crystallization of PLLA on cooling at 1 °C/min. At BS content of 1.5 wt % in PLLA matrix, the highest effectiveness of crystallization process was observed, this result was further demonstrated by X-ray diffraction analysis of non-isothermal crystallization behavior at different cooling rate and measurements after isothermal crystallization. X-ray diffraction studies showed also that the addition of BS did not change the crystalline structure of PLLA. Based on the effect of the predetermined melting temperature on the crystallization behavior of PLLA/BS, the optimum process temperature of 190 °C was found. The comparative study on the melting behavior of PLLA/BS composite under different conditions (cooling rate, melting temperature) also confirmed the ability of BS to promote the nucleation of PLLA crystallization. The crystallization of PLLA/BS composite depends on the concentration of BS additive, crystallization temperature and time as well as heating rate.

Keywords: poly(L-lactic acid), salicyloyl hydrazide derivatives, crystallization, melting, nucleation.

Krystalizacja i topnienie poli(kwasu L-mlekowego) modyfikowanego salicyloilową pochodną hydrazydu

Streszczenie: Badano wpływ nowego organicznego czynnika nukleującego, salicyloilowej pochodnej hydrazydu (BS), na krystalizację i topnienie poli(kwasu L-mlekowego) (PLLA). Na podstawie badań metodą różnicowej kalorymetrii skaningowej stwierdzono, że wprowadzenie dodatku BS (0,2–3,0 % mas.) wyraźnie promuje krystalizację PLLA w warunkach chłodzenia z szybkością 1 °C/min. Zawartość 1,5 % mas. BS w osnowie PLLA przyczyniała się do zwiększenia efektywności procesu krystalizacji, co potwierdziły wyniki badań metodą dyfrakcji rentgenowskiej krystalizacji nieizotermicznej w warunkach zmiennej szybkości chłodzenia oraz krystalizacji izotermicznej. Ponadto badania te wykazały, że dodatek BS do PLLA nie zmienia struktury krystalicznej poli(kwasu L-mlekowego). Na podstawie wpływu ustalonych warunków topnienia na przebieg krystalizacji PLLA/BS stwierdzono też, że optymalna temperatura tego procesu wynosi 190 °C. Badania porównawcze topnienia kompozytu PLLA/BS w różnych warunkach (szybkości chłodzenia, temperatury topnienia) również wskazują na zdolność BS do zarodkowania krystalizacji PLLA. Stwierdzono, że krystalizacja kompozytu PLLA/BS zależy od stężenia dodatku BS, temperatury krystalizacji, czasu krystalizacji i szybkości ogrzewania próbki.

Słowa kluczowe: poli(kwas L-mlekowy), salicyloilowe pochodne hydrazydu, krystalizacja, topnienie, nukleacja.

White pollution is defined as waste plastics that are derived from the petroleum-based polymers such as polystyrene, polypropylene, poly(vinyl chloride), *etc.* It has seriously affected our living environment. Thus, a replacement for petroleum-based polymers using degradable bio-based polymers is very necessary to reduce the white pollution and maintain low carbon emissions. Poly(L-lactic acid) (PLLA) as a typical bio-based plastic, in comparison to other bio-based polymers, exhibits the most promising alternatives for commercial traditional plastic, resulting from its excellent biocompatibility, biodegradability, as well as melt-processability [1–3]. As a result of the continuous research for PLLA, many functional materials based on PLLA were fabricated to attempt their applications in various fields [4, 5]. For example,

---

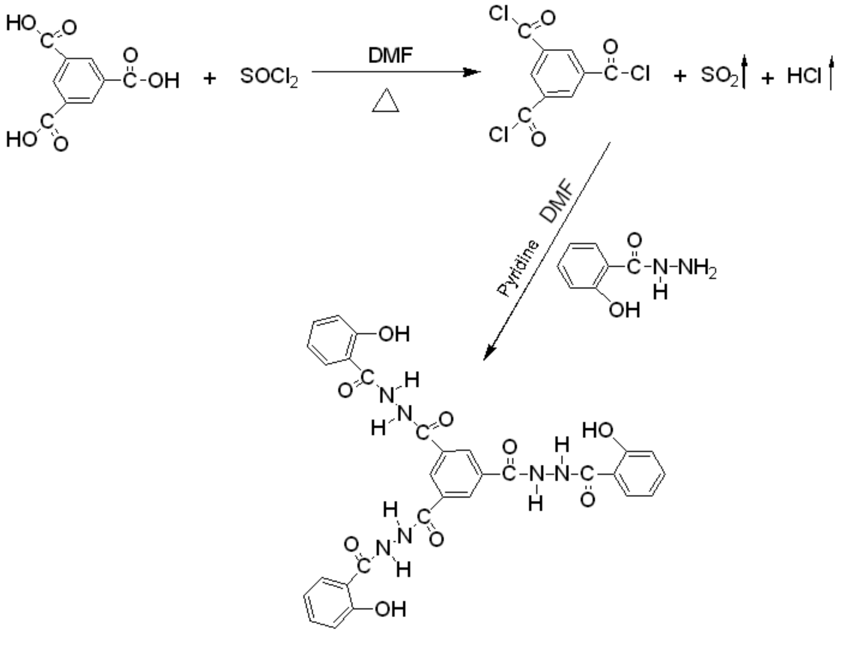
1) Chongqing Key Laboratory of Environmental Materials & Remediation Technologies, Chongqing University of Arts and Sciences, Chongqing-402160, P.R. China.

*) Authors for correspondence; e-mail: caiyh651@aliyun.com and tianll07@163.com

PLLA/multiwalled carbon nanotubes nanocomposite foams with low-density, low thickness, and high conductivity were facilely prepared using a combinatorial technology of pressure-induced flow processing and supercritical carbon dioxide foaming to be firstly used as electromagnetic interference shielding material. The relevant data showed that this nanocomposite foams presented excellent electrical conductivity and electromagnetic interference shielding properties, exhibiting the potential application in electronics, automobiles and packaging [6]. Lou and coworkers [7] from Qingdao University of China fabricated the PLLA/chitosan fiber composite scaffolds *via* combining thermal induced phase separation and salt leaching techniques. This composite scaffolds had high porosity and hierarchical pore structure comprised of 50 nm–10 μm micropores and 50–300 μm macropores, and as it was shown by cell culture experiments, PLLA/chitosan fiber composite scaffolds supported MG-63 osteoblast proliferation and penetration.

The low crystallinity of the virgin PLLA itself, resulting from small concentrations of D-lactic acid in lactic acid monomer, leads to the low heat distortion temperature [8], which is a major challenge for PLLA application. Usually, PLLA has high heat distortion temperature after full crystallization, the reason is that a regular structure needs to expend more energy to destroy it, thereby enhancing the heat resistance [9]. Accordingly, accelerating the crystallization of PLLA on cooling to increase the crystallinity is required. Up to now, adding the nucleating agent is still the most effective way to promote the crystallization of PLLA [10, 11], and therefore, nucleating agents for PLLA have been a subject of great interest in recent years [12–17]. At the initial stage, these studies focused on the use of layered silicates such as talc [18], montmorillonite [19], fluorine mica [20], *etc*. Then the nucleating agents gradually evolved into nano-inorganic salt [21], nano-oxide [22], nano-carbon materials [23, 24] with the rapid development of nanotechnology as well as synthetic inorganic compounds including WS_2 nanotubes [25], zinc phenylphosphonate [26], cadmium phenylmalonate [27], MgO whiskers [28], *etc*. Although these inorganic nucleating agents exhibit strong accelerating effects for PLLA crystallization, they can not still meet the industrial requirements and, what is worse, the surface modification often needs to be performed to increase the compatibility between inorganic nucleating agents and PLLA matrix, resulting in more complex process and higher manufacturing costs. On the other hand, it is more difficult to design more novel inorganic nucleating agents, compared with organic nucleating agents.

Recently, many novel synthetic organic compounds, such as bisurea derivatives [29], benzoyl hydrazine derivatives [30, 31], polyhedral oligomeric silsequioxane derivatives [32], 1H-benzotriazole derivatives [33, 34], were employed to serve as the nucleating agents for PLLA. And, compared to the inorganic counterparts, the advantages including a designable structure and excellent compatibility cause organic nucleating agents to exhibit more promising application in PLLA matrix. Moreover, the relationship between organic group and nucleation effectiveness is being gradually revealed with synthesis of more organic nucleating agents. The number of organic nucleating agent, however, is still limited. Thus, in the current work, as far as our knowledge is concerned, *N,N,N′*-tris(salicyloyl) trimesic acid hydrazide (designated in this work as BS), an aromatic salicyloyl hydrazide derivative, was synthesized to be firstly used as a nucleating agent for PLLA to manipulate the crystallization. Also, the thermal properties of PLLA with different aromatic salicyloyl hydrazide derivative concentration were investigated in terms of crystallization behavior, melting behavior, thermal stability as well as optical performance.



Scheme A

EXPERIMENTAL PART

Materials

PLLA used in this work, trademark 2002D, was purchased from Nature Works LLC, USA. Salicyloyl hydrazide and trimesic acid were obtained from Shanghai Titan Scientific Co. Ltd and Chongqing Huangwei Chemical Reagents Company, respectively. Thionyl dichloride, pyridine and *N,N*-dimethylacetamide were procured from Mianyang Rongshen Chemical Reagents Company.

Synthesis of BS

The synthetic route of BS is shown in Scheme A. First, the tris-chloride was synthesized according to our previous work [35], then the salicyloyl hydrazide was dissolved in *N,N*-dimethylacetamide through ultrasonic cleaner, and the tris-chloride was added slowly into the mixed solution under nitrogen atmosphere, followed by adding pyridine, the mixture was stirred for 2 h at room temperature, heated up to 70 °C to maintain the reaction for 3 h. Finally, the reaction mixture was poured into 400 cm^3 water to filtrate, and the aforementioned procedure was operated for 3 times. The resulting product was dried in vacuum at 45 °C for 24 h.

IR (KBr) υ: 3450.9, 3314.2, 1639.8, 1608, 1544.6, 1486.2, 1456.7, 1430.3, 1376.4, 1283.9, 1235.3, 1159.6, 1101.5, 1307.3, 907.2, 857.1, 754.6, 668.9 cm^{-1};

^{1}H NMR (DMSO, 400 MHz) δ: ppm; 11.89 (s, 1H, OH), 11.07 (s, 1H, NH), 10.82 (s, 1H, NH), 6.97~8.67 (m, 5H, Ar).

Preparation of PLLA/BS samples

PLLA and BS were blended using RM-200C torque rheometer (Harbin Hapro Electric Technology Go., Ltd., China). The blending parameters were: a rotation speed of 32 rpm for 7 min at 180 °C, and of 64 rpm for 7 min. Then the blends were hot pressed and cool pressed for 5 min and 10 min, respectively, to prepare sheets with a thickness of approximately 0.4 mm.

Methods of testing

– FT-IR spectra of BS were performed by a Bio-Rad FTS135 spectrophotometer from 4000 to 400 cm^{-1}; and the ^{1}H NMR spectra was recorded on Brucker AVANCE 400 MHz spectrometers, the deuterated solvent was DMSO.

– The non-isothermal crystallization and melting behavior under different circumstances were analyzed by TA Instruments Q2000 DSC under nitrogen at a rate of 50 cm^3/min.

– X-ray diffraction (XRD) experiments after isothermal crystallization were performed on a D/MAX2550 diffractometer using Cu K$_\alpha$ radiation at room temperature in the range of 2θ = 5–60° with scanning rate of 2 °/min.

– The thermogravimetric properties were tested on TA Instruments Q500 TGA in a flow of air (60 cm^3/min) from room temperature to 650 °C at a heating rate of 5 °C/min.

RESULTS AND DISCUSSION

Crystallization behavior

A comparative study on non-isothermal crystallization behavior of the virgin PLLA and BS-modified PLLA was firstly investigated to evaluate the nucleating effectiveness of BS.

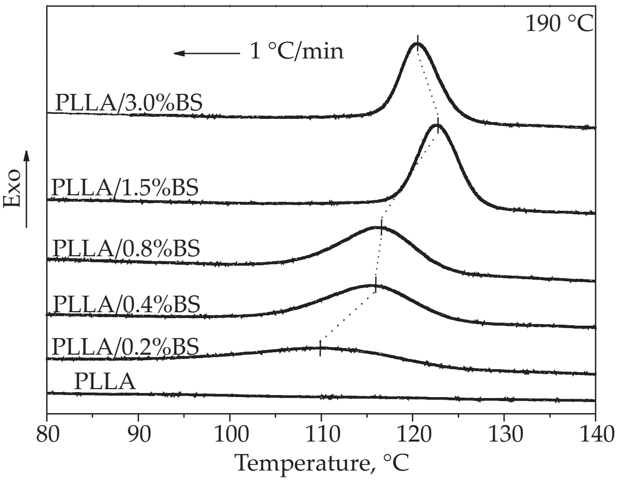


Fig. 1. DSC curves of the virgin PLLA and PLLA/BS samples from the melt at a cooling rate of 1 °C/min

Figure 1 shows the non-isothermal crystallization curves of the virgin PLLA and PLLA/BS samples from the melt (190 °C) at a cooling rate of 1 °C/min. As reported in the literature [9, 36, 37] and shown in Fig. 1, the virgin PLLA has almost no discernible non-isothermal crystallization peak in cooling, which indicates that the cooling rate of 1 °C/min is too fast for the virgin PLLA to crystallize and shows a poor crystallization ability of PLLA itself. In contrast, all PLLA/BS samples exhibit the apparent non-isothermal crystallization peak, suggesting that the presence of BS promotes the crystallization of PLLA on cooling [15]. That is to say, BS can act as an effective site of heterogeneous nucleation, resulting in the increase of nucleation density and subsequently promoting the crystallization on cooling. In addition, when the BS concentration is 0.2–1.5 wt %, it is observed that the non-isothermal crystallization peak shifts to higher temperature with the increase of BS loading, the reason still depends on the increasing induced-crystallization effectiveness of BS. However, when the BS concentration is more than 1.5 wt %, the non-isothermal crystallization peak shifts to low temperature, the similar result has been reported for PLA nucleated by phthalimide [38]. This also indicates that BS should not be overloaded, otherwise, the excessive BS may inhibit the mobility of PLLA chains segment, resulting in the decrease of crystallization performance.

Table 1. DSC data of the virgin PLLA and PLLA/BS samples from the melt at a cooling rate of 1 °C/min

Sample	T_o, °C	T_{cp}, °C	ΔH_c, J/g
PLLA	101.4	94.5	0.1
PLLA/0.2%BS	123.9	110.2	24.6
PLLA/0.4%BS	124.3	115.3	33.2
PLLA/0.8%BS	123.6	116.2	33.1
PLLA/1.5%BS	127.1	122.6	34.9
PLLA/3.0%BS	124.9	120.4	33.7

The crystallization of PLLA depends on two factors, nucleation and crystal growth [11], under this circumstance the inhibiting effect for the mobility of PLLA chains segment is predominant, compared to the nucleating effect of BS. Thus, we suggest that 1.5 wt % BS offers the best accelerating effect for the crystallization of PLLA.

The relevant DSC data (see Table 1) also showed that PLLA/1.5%BS exhibits the highest onset crystallization temperature (T_o) 127.1 °C, the crystallization peak temperature (T_{cp}) 122.6 °C, and the largest the non-isothermal crystallization enthalpy (ΔH_c) 34.9 J/g.

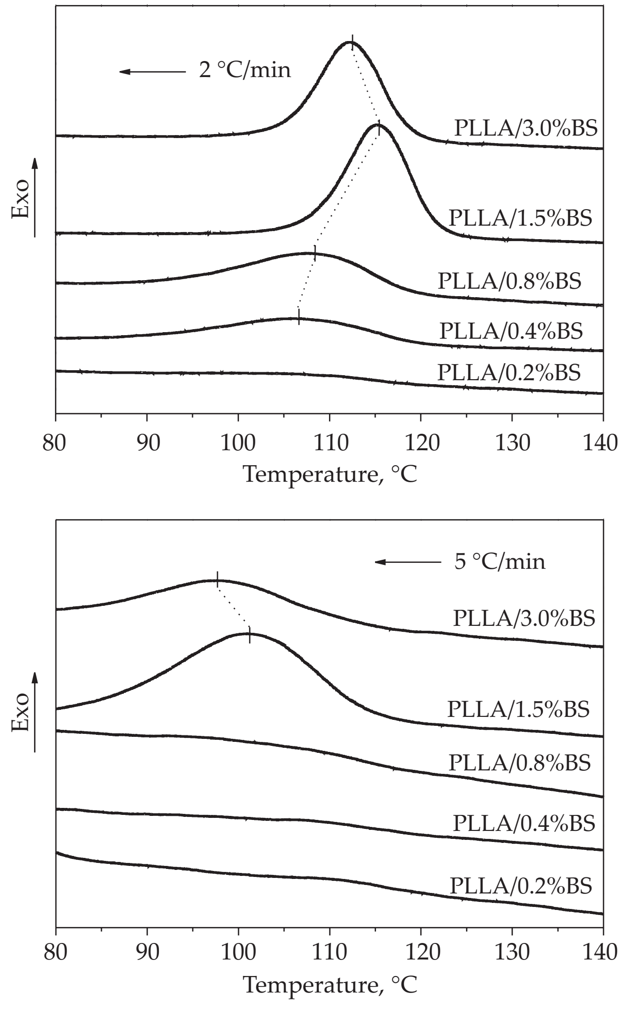


Fig. 2. DSC curves of PLLA/BS samples at different cooling rate

As reported by many authors [27, 39–41], the cooling rate could significantly affect the non-isothermal crystallization. In the non-isothermal crystallization section, we also investigated the effect of cooling rate on the crystallization behavior of PLLA/BS.

Figure 2 presents the DSC curves of PLLA/BS samples from the melt at different cooling rate. It is clear that DSC curves at these cooling rates are drastically different from that at a cooling rate of 1 °C/min. With the increase of cooling rate, the non-isothermal crystallization peaks become wide, shift to lower temperature and even gradually disappear. Upon cooling at 2 °C/min, the non-isothermal crystallization peak of PLLA/0.2%BS can almost not be observed, suggesting that cooling rate of 2 °C/min exhibits stronger weakening effect on the crystallization of PLLA in cooling, compared to the crystallization promoting effect of 0.2 wt % BS for PLLA. In addition, the non-isothermal crystallization peaks of PLLA/0.4%BS and PLLA/0.8%BS disappear at a cooling rate of 5 °C/min. However, PLLA/1.5%BS and PLLA/3.0%BS still have obvious non-isothermal crystallization peak, this result is consistent with the aforementioned non-isothermal crystallization DSC data. Moreover, the non-isothermal crystallization peak of PLLA/1.5%BS is sharper than that of PLLA/3.0%BS, and the crystallization peak temperature is higher, further indicating the 1.5 wt % BS is the optimal concentration for achieving the best nucleation performance for PLLA.

According to the rule: "like dissolves like", a small amount of BS must be dissolved in PLLA matrix during processing, and the rest of undissolved BS will become the nuclei to PLLA crystallization. However, because the solubility of BS in PLLA matrix is different at different predetermined final melting temperature (T_{sm}), it would directly affect the nucleating density and compatibility. The study on influence of the T_{sm} on the crystallization behavior may be necessary to explore the optimal processing parameters.

Figure 3 depicts the DSC curves of PLLA/BS samples from the different T_{sm} at a cooling rate of 1 °C/min. From Fig. 1 and Fig. 3 it is clear that the T_{cp} increases at first, then decreases at various T_{sm} from 180 °C to 200 °C, and when the T_{sm} is 190 °C, all PLLA/BS samples exhibit the highest T_{cp}, showing that 190 °C is the optimization processing temperature. The probable reason of this trend is that when the T_{sm} is 180 °C, only a tiny amounts of BS are dissolved in PLLA matrix because of low T_{sm}, leading to slightly poor compatibility and weak interaction between undissolved BS and PLLA. Whereas when the T_{sm} is 200 °C, although the compatibility and interaction between undissolved BS and PLLA may be significantly enhanced, PLLA starts its thermal decomposition [42], and the appearance of a small molecular chain segment is not beneficial to crystallization on cooling, resulting from its greater capacity for movement and weaker nucleating ability. Moreover, on the basis of the analysis of T_{cp} at dif-

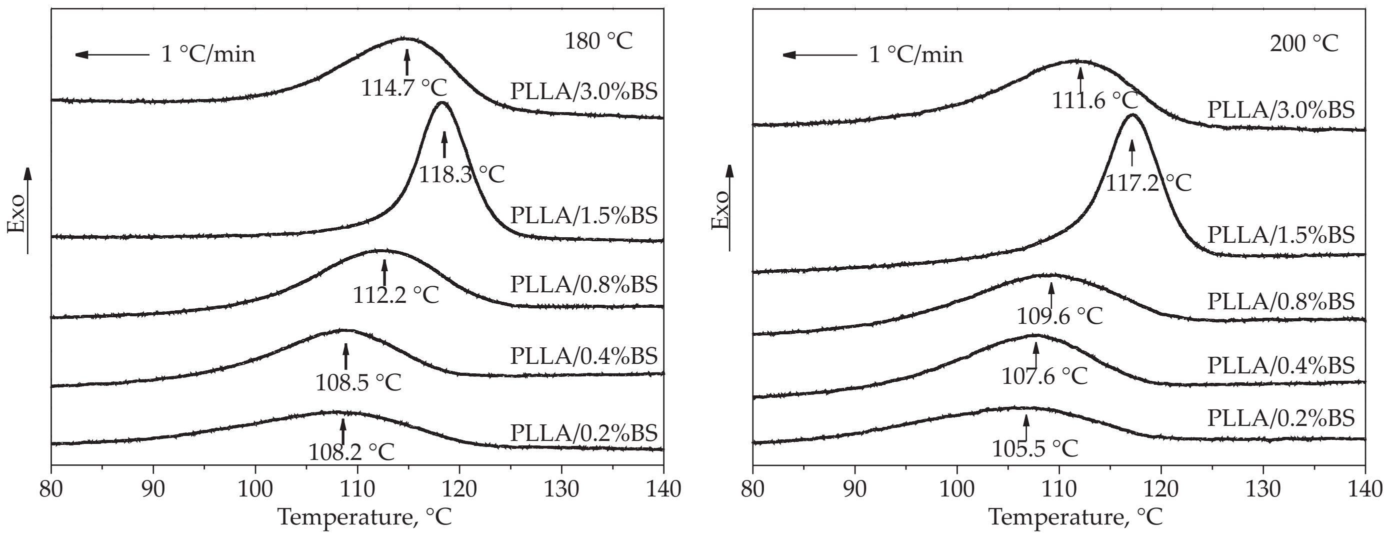


Fig. 3. DSC curves of PLLA/BS samples from different predetermined final melting temperature (T_{sm}) at a cooling rate of 1 °C/min

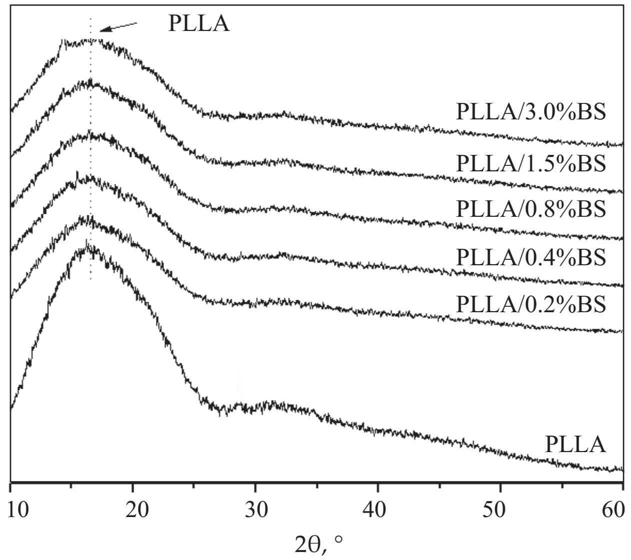


Fig. 4. XRD curves of the virgin PLLA and PLLA/BS samples without crystallization treatment

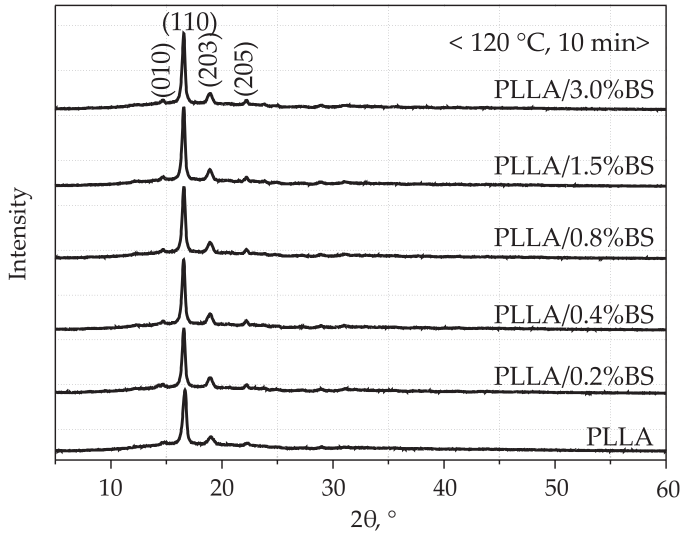


Fig. 5. XRD curves of the virgin PLLA and PLLA/BS samples after heat treatment at 120 °C for 10 min

ferent T_{sm}, it was found that the maximum difference of the same PLLA/BS sample at different T_{sm} reaches 8.8 °C, fully confirming that the T_{sm} can affect the non-isothermal crystallization behavior of PLLA/BS.

Usually, the semicrystalline polymers can exhibit the stronger X-diffraction peak after crystallization [43]. Thus, investigating the crystallization behavior using XRD is feasible.

Figure 4 presents the XRD patterns of the virgin PLLA and PLLA/BS samples without crystallization, whereas Fig. 5 shows the XRD curves of the virgin PLLA and PLLA/BS samples after heat treatment at 120 °C for 10 min. It is clear from Fig. 4 that both the virgin PLLA and PLLA/BS samples only exhibit a flat and very wide diffraction peak, resulting from their amorphous character. In contrast, after heat treatment, there are four peaks observed in XRD pattern of all samples, the (010), (110), (203), and (205) diffraction peaks at 2θ = 14.7°, 16.6°, 18.9°, and 22.2° [44], including the virgin PLLA and PLLA/BS samples. These peaks become sharper as a result of the existence of PLLA crystals. Furthermore, the variation trend of diffraction intensity of the virgin PLLA and PLLA with different BS concentration is similar to the results shown in Table 1. That is, the virgin PLLA exhibits the minimum diffraction peak, and PLLA/1.5%BS has the larger diffraction peak. As a result, XRD measurements reveal that the incorporation of BS promotes the crystallization of PLLA again but can not contribute to any change in crystalline structure.

Melting behavior

After non-isothermal crystallization, the following melting behavior during the second heating scan must reflect the primary crystallites formed on cooling and role of BS.

Figure 6 displays the melting behavior of the virgin PLLA and PLLA/BS samples after non-isothermal cry-

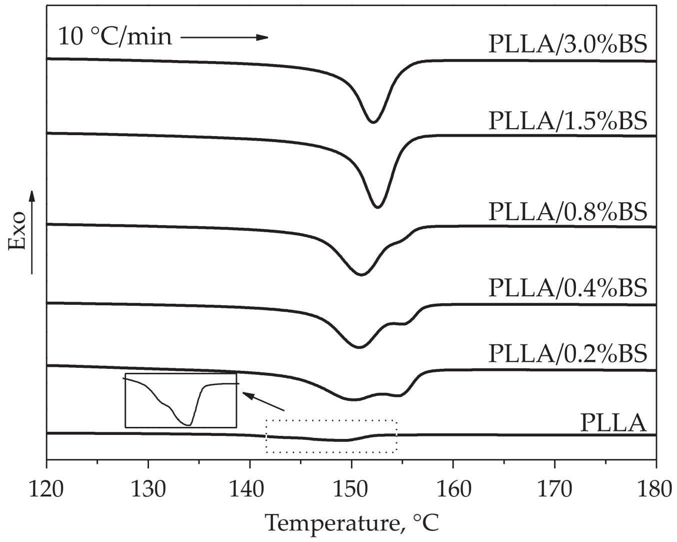


Fig. 6. Melting behavior of the virgin PLLA and PLLA/BS samples after non-isothermal crystallization

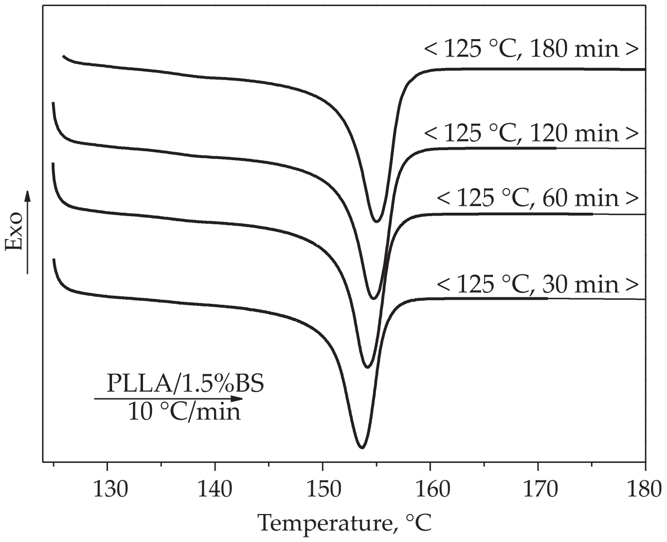


Fig. 7. Melting behavior of PLLA/1.5%BS at a heating rate of 10 °C/min after isothermality for different time at 125 °C

stallization at a cooling rate of 1 °C/min. As seen in Fig. 6, the melting peak of the virgin PLLA is very weak, showing that PLLA can almost not form crystal on cooling. Also the second heating scan demonstrates the poor crystallization ability of the virgin PLLA. In comparison to the virgin PLLA, PLLA/BS samples appear the typical and obvious melting peak, indicating that the existence of BS accelerates the crystallization of PLLA under the same conditions. Besides, the melting behavior of PLLA/BS samples greatly depend on BS concentration in PLLA matrix. With the increase of BS concentration, for PLLA/BS system, the double melting peak gradually converts into the single melting peak. When the BS concentration is 0.2–0.8 wt %, the nucleating density does not saturate on cooling, leading to the formation of new crystals during the heating scan, finally resulting in the appearance of double melting peaks according to the melting-recrystallization mechanism [45]. However, when the BS concentration is in the range of 1.5–3 wt % , the nucleating density in PLLA matrix is saturated, and the crystallization has been completed on cooling. Consequently the crystallization does not to occur during the second heating scan, forming the single melting peak. Meanwhile, the single melting peak of PLLA/1.5%BS is sharper than that of PLLA/3.0%BS, showing that the crystals formed on cooling, for PLLA/1.5%BS, are more perfect. On one hand, the rapid formed crystals through BS suffer from more defects, in particular, overmuch BS can supply enough nucleation site; on the other hand, as aforementioned, the excessive BS hinders the growth of crystals leading to the formation of more imperfect crystals on cooling. This result further evidences the best nucleating effect of 1.5 wt % BS.

As indicated by the aforementioned results for non-isothermal crystallization section, 1.5 wt % BS is the best crystallization promoter for PLLA. Hence, the fol-

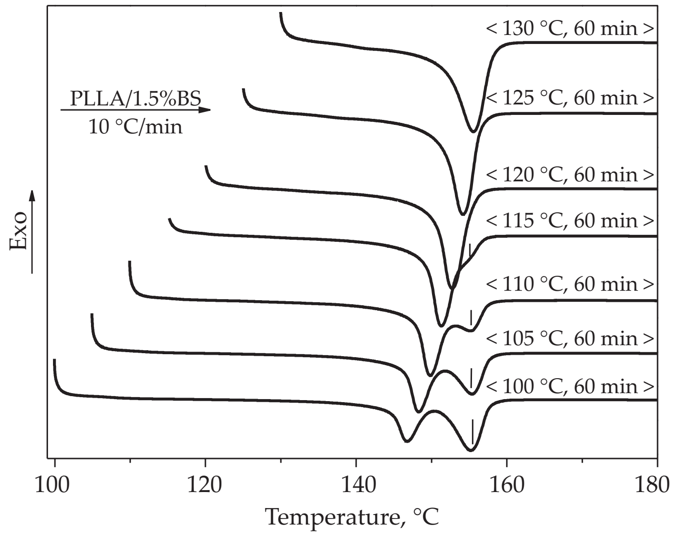


Fig. 8. Melting behavior of PLLA after isothermality for 60 min at different crystallization temperature

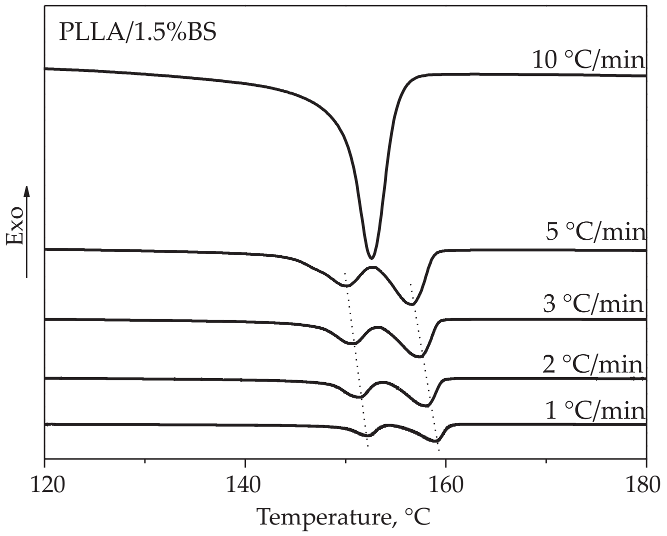


Fig. 9. Melting behavior of PLLA/BS at a different heating rate after non-isothermal crystallization

lowing investigation on the melting behavior focuses on the PLLA/1.5%BS system.

Figure 7 illustrates the melting behavior of PLLA /1.5%BS at a heating rate of 10 °C/min after isothermality for different time at 125 °C. As shown in Fig. 7, only one single melting peak exists, although the isothermal time is different, showing that there are no regenerated crystals in heating. Usually, the longer the isothermal time is, the more perfect the crystals are in the high crystallization temperature zone, thus, the longer isothermal time causes the melting peak to shift to the higher temperature.

As it is shown in Fig. 7 PLLA/1.5%BS has only one melting peak after isothermality for 60 min at high crystallization temperature (125 °C). However, the crystal growth rate is crucial in low crystallization temperature zone, compared to the nuclear rate, very possibly resulting in a different melting behavior.

Figure 8 shows the melting behavior of PLLA after isothermality for 60 min at different crystallization temperature. It is clear that double melting peaks appear in low crystallization temperature regions, and the single melting peak occurs in high crystallization temperature zone, and the high temperature melting peak, for double melting peaks, gradually degenerates into the single melting peak with the increase of crystallization temperature. The appearance of double melting peaks results from the recrystallization of PLLA/1.5%BS on heating. In low crystallization temperature regions, the macromolecular segment active ability is poor and the crystal rapidly formed through BS is imperfect. Its further growth on heating results in the difference in the degree of crystal perfection. In addition, for double melting peaks, the high temperature melting peak does not move, whereas the low temperature melting peak shifts to higher temperature with the increase of crystallization temperature, indicating that the crystals are more perfect at higher crystallization temperature.

In the above section, crystallization temperature presents a significant effect on the melting behavior of PLLA/BS. Similarly, many authors [46–48] reported that the heating rate also affect the melting behavior, therefore, the effect of heating rate on the melting behavior of PLLA/BS after non-isothermal crystallization was investigated (see Fig. 9).

When the heating rate is no more than 5 °C/min, PLLA/1.5%BS exhibits the double melting peaks, which shift to lower temperature with the increase of heating rate. Moreover, the drop level of both low temperature melting peak and high temperature melting peak is consistent with the increase of heating rate, this result may be of interest to investigate the relationship between crystallization and the following heating. Although PLLA/1.5%BS exhibits the same crystallization during non-isothermal crystallization of 1 °C/min, the different heating rate in the second heating scan consequently affects the primary crystallites according to the results shown in Fig. 9. When the heating rate is more than 5 °C/min, the double melting peaks merge into the large single melting peak. The reason is that the high heating rate makes the low temperature melting peak undergo thermal hysteresis, and the heating rate is predominant under this circumstance.

CONCLUSIONS

BS was synthesized from salicyloyl hydrazide and tris-chloride which was prepared from trimesic acid *via* acylation, and BS-nucleated PLLA was fabricated *via* melt-blending technology to evaluate the effect of BS on the crystallization and melting behavior of PLLA through DSC and XRD. Both non-isothermal crystallization and XRD results after isothermal crystallization showed that BS could act as a powerful crystallization promoter in PLLA crystallization. Compared to the virgin PLLA, at the optimum concentration of 1.5 wt % BS, the T_o, T_{cp}, and ΔH_c increased from 101.4 °C, 94.5 °C, and 0.1 J/g to 127.1 °C, 122.6 °C, and 34.9 J/g, respectively. The relevant measurements indicated that the cooling rate and predetermined final melting temperature could affect significantly the non-isothermal crystallization behavior of PLLA/BS system. The increase of cooling rate would weakened the crystallization promoting effectiveness of BS, and caused the non-isothermal crystallization peak to become wide and shift to lower temperature. The effect of the predetermined final melting temperature on non-isothermal crystallization behavior suggested that 190 °C was the optimum processing temperature for PLLA/BS system, and PLLA/BS had the highest T_{cp} at 190 °C. The difference in the melting behavior of the virgin PLLA and PLLA/BS samples further confirmed the role of BS in the promotion of PLLA crystallization. Besides, the BS concentration, crystallization temperature and time, as well as heating rate are key factors for the melting behavior of PLLA/BS system.

This work was supported by National Natural Science Foundation of China (project number 51403027), Natural Science Foundation of Chongqing Municipal Science and Technology Commission (project number cstc2015jcyjBX0123), Scientific and Technological Research Program of Chongqing Municipal Education Commission (project number KJ1601101), and Innovation Team Project of Chongqing Municipal Education Commission (project number CXTDX201601037).

REFERENCES

[1] Nagarajan V., Mohanty A.K., Misra M.: *Journal of Applied Polymer Science* **2016**, *133*, 43 673.
http://dx.doi.org/10.1002/app.43673

[2] Wang J.Y., Bai J., Zhang Y.Q. *et al.*: *Scientific Reports* **2016**, *6*, 26 560.
http://dx.doi.org/10.1038/srep26560

[3] Lizundia E., Fortunati E., Dominici F. *et al.*: *Carbohydrate Polymers* **2016**, *142*, 105.

http://dx.doi.org/10.1016/j.carbpol.2016.01.041

[4] Luo B.H., Wang S.Q., Rao R. *et al.*: *Nanoscale Research Letters* **2016**, *11*, 227.
http://dx.doi.org/10.1186/s11671-016-1421-x

[5] Kathuria A., Abiad M.G., Auras R.: *Polymer* **2013**, *54*, 6979.
http://dx.doi.org/10.1016/j.polymer.2013.11.005

[6] Kuang T.R., Chang L.Q., Chen F. *et al.*: *Carbon* **2016**, *105*, 305.
http://dx.doi.org/10.1016/j.carbon.2016.04.052

[7] Lou T., Wang X.J., Yan X. *et al.*: *Materials Science & Engineering C – Materials for Biological Applications* **2016**, *64*, 341.
http://dx.doi.org/10.1016/j.msec.2016.03.107

[8] Jalali A., Huneault M.A., Eikoun S.: *Journal of Materials Science* **2016**, *51*, 7768.
http://dx.doi.org/10.1007/s10853-016-0059-5

[9] Fan Y.Q., Yu Z.Y., Cai Y.H. *et al.*: *Polymer International* **2013**, *62*, 647.
http://dx.doi.org/10.1002/pi.4342

[10] Cai Y.H., Yan S.F., Yin J.B. *et al.*: *Journal of Applied Polymer Science* **2011**, *121*, 1408.
http://dx.doi.org/10.1002/app.33633

[11] Fan Y.Q., Zhu J., Yan S.F. *et al.*: *Polymer* **2015**, *67*, 63.
http://dx.doi.org/10.1016/j.polymer.2015.04.062

[12] Kesenci K., Fambri L., Migliaresi C. *et al.*: *Journal of Biomaterials Science – Polymer Edition* **2000**, *11*, 617.
http://dx.doi.org/10.1163/156856200743904

[13] Wen L.A., Xin Z.: *Chinese Journal of Chemical Engineering* **2010**, *18*, 899.
http://dx.doi.org/10.1016/S1004-9541(09)60145-2

[14] Qiu Z.B., Li Z.S.: *Industrial & Engineering Chemistry Research* **2011**, *50*, 12 299.
http://dx.doi.org/10.1021/ie2019596

[15] Shi Y.Y., Shao L.N., Yang J.H. *et al.*: *Polymers for Advanced Technologies* **2013**, *24*, 42.
http://dx.doi.org/10.1002/pat.3047

[16] Sun Z.Q., Zhang H., Pang X. *et al.*: *Chemical Research in Chinese Universities* **2014**, *30*, 333.
http://dx.doi.org/10.1007/s40242-013-3275-4

[17] Xue B., Guo D., Bao J.J.: *Journal of Polymer Engineering* **2016**, *36*, 381.
http://dx.doi.org/10.1515/polyeng-2015-0298

[18] Li H.B., Huneault M.A.: *Polymer* **2007**, *48*, 6855.
http://dx.doi.org/10.1016/j.polymer.2007.09.020

[19] Nam P.H., Ninomiya N., Fujimori A. *et al.*: *Polymer Engineering and Science* **2006**, *46*, 39.
http://dx.doi.org/10.1002/pen.20436

[20] Ray S.S., Yamada K., Ogami A. *et al.*: *Macromolecular Rapid Communications* **2002**, *23*, 943.
http://dx.doi.org/10.1002/1521--3927(200211)23:16<943::AID-MARC943>3.0.CO;2-F

[21] Han L.J., Han C.Y., Bian J.J. *et al.*: *Polymer Engineering and Science* **2012**, *52*, 1474.
http://dx.doi.org/10.1002/pen.23095

[22] Li Y.H., Chen C.H., Li J. *et al.*: *Journal of Applied Polymer Science* **2012**, *124*, 2968.
http://dx.doi.org/10.1002/app.35326

[23] Kim S.Y., Shin K.S., Lee S.H. *et al.*: *Fibers and Polymer* **2010**, *11*, 1018.
http://dx.doi.org/10.1007/s12221-010-1018-4

[24] Chen L., Pang X.J., Yu G.S. *et al.*: *Composites Science and Technology* **2013**, *74*, 160.
http://dx.doi.org/10.1016/j.compscitech.2012.11.007

[25] Naffakh M., Marco C.: *Journal of Materials Science* **2015**, *50*, 6066.
http://dx.doi.org/10.1007/s10853-015-9156-0

[26] Han L.L., Pan P.J., Shan G.R. *et al.*: *Polymer* **2015**, *63*, 144.
http://dx.doi.org/10.1016/j.polymer.2015.02.053

[27] Li C.L., Dou Q., Bai Z.F. *et al.*: *Journal of Thermal Analysis and Calorimetry* **2015**, *122*, 407.
http://dx.doi.org/10.1007/s10973-015-4677-y

[28] Zhao Y., Liu B., You C. *et al.*: *Materials and Design* **2016**, *89*, 573.
http://dx.doi.org/10.1016/j.matdes.2015.09.157

[29] Xu Y.T., Wu L.B.: *European Polymer Journal* **2013**, *49*, 865.
http://dx.doi.org/10.1016/j.eurpolymj.2012.12.015

[30] Bai H.W., Huang C.M., Xiu H. *et al.*: *Polymer* **2014**, *55*, 6924.
http://dx.doi.org/10.1016/j.polymer.2014.10.059

[31] Zou G.X., Jiao Q.W., Zhang X. *et al.*: *Journal of Applied Polymer Science* **2015**, *132*, 41 367.
http://dx.doi.org/10.1002/app.41367

[32] Fernandez M.D., Fernandez M.J., Cobos M.: *Journal of Materials Science* **2016**, *51*, 3628.
http://dx.doi.org/10.1007/s10853-015-9686-5

[33] Cai Y.H., Tang Y., Zhao L.S.: *Journal of Applied Polymer Science* **2015**, *132*, 42 402.
http://dx.doi.org/10.1002/app.42402

[34] Cai Y.H., Zhao L.S., Zhang Y.H.: *Journal of Polymer Research* **2015**, *22*, 246.
http://dx.doi.org/10.1007/s10965-015-0887-z

[35] Cai Y.H., Zhang Y.H.: *Advances in Materials Science and Engineering* **2014**, *2014*, 843 564.
http://dx.doi.org/10.1155/2014/843564

[36] Zhang R., Wang Y.M., Wang K.J. *et al.*: *Polymer Bulletin* **2013**, *70*, 195.
http://dx.doi.org/10.1007/s00289-012-0814-y

[37] Ma P.M., Xu Y.S., Wang D.W. *et al.*: *Industrial & Engineering Chemistry Research* **2014**, *53*, 12 888.
http://dx.doi.org/10.1021/ie502211j

[38] He D.R., Wang Y.M., Shao C.G. *et al.*: *Polymer Testing* **2013**, *32*, 1088.
http://dx.doi.org/10.1016/j.polymertesting.2013.06.005

[39] Liu Y.F., Wang L., He Y. *et al.*: *Polymer International* **2010**, *59*, 1616.
http://dx.doi.org/10.1002/pi.2894

[40] Su Z.Z., Guo W.H., Liu Y.J. *et al.*: *Polymer Bulletin* **2009**, *62*, 629.
http://dx.doi.org/10.1007/s00289-009-0047-x

[41] Chen H.M., Zhang W.B., Du X.C. *et al.*: *Thermochimica Acta* **2013**, *566*, 57.

http://dx.doi.org/10.1016/j.tca.2013.05.018
[42] Song J.: *Sichuan Chemical Industry* **1994**, S2, 38, (in Chinese).
[43] Li Y.L., Wang Y., Liu L. *et al.*: *Journal of Polymer Science Part B: Polymer Physics* **2009**, *47*, 326. http://dx.doi.org/10.1002/polb.21645
[44] Hergeth W.D., Lebek W., Stettin E. *et al.*: *Die Makromolekulare Chemie* **1992**, *193*, 1607.
[45] Cai Y.H.: *South African Journal of Chemistry – Suid-Afrikaanse Tydskrif vir Chemie* **2011**, *64*, 115.
[46] Shi Q.F., Mou H.Y., Gao L. *et al.*: *Journal of Polymers and the Environment* **2010**, *18*, 567. http://dx.doi.org/10.1007/s10924-010-0252-6
[47] Su Z.Z., Li Q.Y., Liu Y.J. *et al.*: *Journal of Polymer Science Part B: Polymer Physics* **2009**, *47*, 1971. http://dx.doi.org/10.1002/polb.21790
[48] Huang J.W., Hung Y.C., Wen Y.L. *et al.*: *Journal of Applied Polymer Science* **2009**, *112*, 3149. http://dx.doi.org/10.1002/app.29699

Received 12 XII 2016.

WROCŁAWSKIE CENTRUM BADAŃ EIT+

zaprasza na pierwsze seminarium

„Bezpieczeństwo stosowania materiałów w produktach innowacyjnych – NANOTOX"

Wrocław, 24 października 2017 r.

Rosnąca popularność nanomateriałów oraz ich obecność w innowacyjnych produktach i niemal w każdej dziedzinie życia, wymaga rzetelnej wiedzy na temat bezpieczeństwa ich stosowania oraz ich wpływu na środowisko. Ogromne znaczenie ma zatem przedstawienie potencjalnych zagrożeń wynikających ze stosowania tych materiałów oraz sprawdzonych metod badawczych do oceny ich właściwości.

Tematyka:

- „Nanotechnologia i nanomateriały – definicje, odmienne właściwości, wytwarzanie nanocząstek o określonych właściwościach" (EIT+)
- „Polskie i Europejskie normy prawne dotyczące wytwarzania i komercyjnego stosowania nanomateriałów, bezpieczeństwo pracy z nanomateriałami" (EIT+)
- „Zastosowania nanomateriałów w przemyśle" (prezentacja firmy NanoPure)
- „Metody charakteryzacji nanomateriałów – charakteryzacja fizykochemiczna, charakteryzacja nanotoksykologiczna" (EIT+)
- „Certyfikat NanoSop" (prezentacja TUV Sud Polska)

Udział w konferencji jest bezpłatny.
Zgłoszenia prosimy wysyłać na adres mailowy: komunikacja@eitplus.pl.
Zgłoszenie powinno zawierać: imię i nazwisko, pełną nazwę firmy/instytucji wraz z adresem pocztowym, mail, nr tel.

Miejsce konferencji: Wrocławskie Centrum Badań EIT+, ul. Stabłowicka 147, Wrocław.

Informacje: Anna Kolbe-Penek, tel. +48 502 397 298, Klaudia Piątek: +40 519 186 532, e-mail: komunikacja@eitplus.pl