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Facile suspension flame spray fabrication of polylactic acid-povidone-iodine coatings for antimicrobial applications

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ABSTRACT

A facile suspension flame deposition route for fabricating polylactic acid (PLA)-based antimicrobial coatings has been developed in this work. Mixture of povidone-iodine (PVP-I) solution and PLA particles was prepared as the starting feedstock to make the PLA-PVP-I composite coatings. Successful fabrication of the PLA-PVP-I coatings were confirmed by microstructure and chemistry analyses. The coatings showed a homogenous structure and smooth topographical features with no visible pores. Well retained chemistry of PLA and uniform dispersion of PVP-I was revealed in the coatings. Antibacterial testing showed remarkable antimicrobial activity of the PLA-PVP-I coatings against both *Escherichia coli* and *Staphylococcus aureus* with a bactericidal rate over 99.99 %, which is likely attributed to the rapid release of iodine. This study provides a promising substrate-independent thermal spray route for constructing antimicrobial coatings for potential biomedical applications.

1. Introduction

Biomaterial-associated infections (BAI) arising from pathogenic microbe contamination is a widespread and rapidly growing problem [1]. According to the survey, the postoperative infection rate in adult intensive care units in developed countries in Europe and America is as high as 4.4 % [2]. Therefore, the construction of antibacterial surface coatings to prevent BAI problems by controlled release of bactericides at early stages is are highly desirable [3]. Polylactic acid (PLA) is a well-known sustainable biomaterial that is likely to be one of the candidates for solving BAI. It's biodegradability and biocompatibility widely used in tissue engineering and medical applications [4–7], but no-desirable antibacterial property greatly limiting the medical application of PLA [8]. Povidone-iodine (PVP-I) that is safe not toxicity to host cells when used at a rational administration of drug [9]. Various studies shown that PVP-I is used to immobilize biomaterials to endow them with antibacterial activity [10]. Therefore, it is expected that the combination of PVP-I with PLA in the form of composite coating, taking advantages of the both components, could be an ideal platform for preventing BAI.

Melt-blown technique, ultrasonic spray and spin coating have been used to fabricate functional coatings with biodegradable polymers. However, those methods may involve some disadvantages such as high cost, difficult operation, uneven and incompact coating, and poisonous substances may be used in the preparation process. Compared with other methods, flame spraying has the advantages of low cost, simple operation and environmental protection. Furthermore, there is no study that employs flame spray to construct biodegradable-polymer based coatings loaded with bactericides for antibacterial applications. Herein, we report a novel technique route to prepare PLA-bactericide composite coatings by suspension flame spray for local delivery of iodine. Physical and chemical composition characterization of the coatings were performed. The release kinetics of iodine from the coatings and its antibacterial effect were also investigated.

2. Experimental materials and methods

2.1. Sample preparation

PLA powders (2035D, Nature Works, USA) with an average molecular weight 50,000 and 200 mesh were suspended in 50:50 (v/v) ethanol/H_2O and thoroughly mixed by stirring 30 % (wt./wt.) PVP-I relative to the PLA powder was dissolved to prepare the PLA-PVP-I coatings. The coatings were deposited by flame spray (CDS 8000, Castolin, Germany) on 316L stainless steel plates with the dimension of 25

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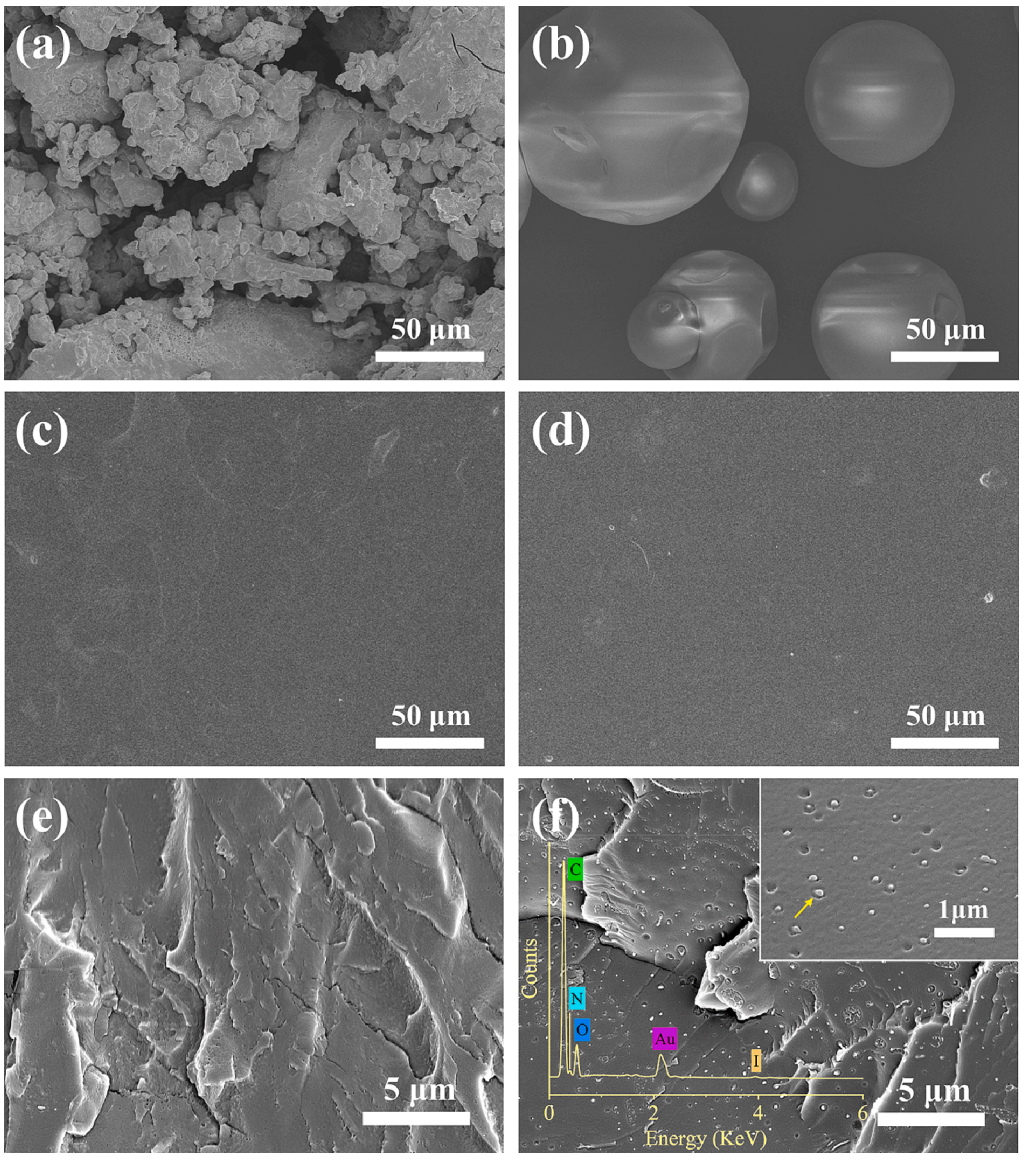

Fig. 1. SEM images of (a) the PLA powder, (b) the PVP-I powder, (c) the PLA coating, (d) the PLA-PVP-I coating, and the fractured surfaces of (e) PLA coating and (f) PLA-PVP-I coating with inset of EDS spectrum and the corresponding magnified image.

× 20 × 1.5 mm. The suspensions were injected into the flame with a homemade spray atomizer. Acetylene was used as the fuel gas with a flow rate of 1.5 Nm^3/h and working pressure of 0.1 MPa. Oxygen was used as the combustion-supporting gas with a flow rate of 2.5 Nm^3/h and working pressure of 0.5 MPa. The spray distance was 200 mm.

2.2. Sample characterization

The microstructure of the powders and coatings was characterized using a field emission scanning electron microscopy (S4800, Hitachi, Japan). Chemical composition of the powders and coatings was determined using X-ray photoelectron spectroscopy (XPS, AXIS ULTRA DLD, Japan). FT-IR spectra were recorded with an Agilent Cary 660 FT-IR spectrometer (Agilent Technologies, Santa Clara, CA, USA). Surface wettability of the composite coatings was evaluated by a water contact angle measurement system (KRUSS, DSA25E, Germany). In order to investigate the release of iodine, they were immersed in 15 mL PBS buffer with gentle shaking at 37 °C. At predetermined time intervals of 1, 2, 4, 8, 12 and 24 h, 1.5 mL solution was collected with 1.5 mL fresh PBS added to the tubes. The iodine content in the PBS solution was determined with inductively coupled plasma optical emission spectroscopy (ICP-OES; SPECTRO ARCOS, SPECTRO Analytical Instruments, Kleve, Germany).

2.3. Antibacterial test

Gram-negative *Escherichia coli* (*E. coli,* ATCC25922) and gram-positive Staphylococcus aureus (*S. aureus*, ATCC6538) were used to determine the antibacterial effects of the coatings. Samples were UV irradiated for 30 min before use. Coating samples were incubated in 6 mL bacteria suspension (~10^6 cells/mL) at 37 °C with gentle shaking for 4 h. Then antibacterial rates were evaluated with a 10-fold serial dilution spread plate method.

3. Results and discussion

The commercially available PLA and PVP-I powders showed a wide size range and irregular morphology (Fig. 1a, b). SEM analysis revealed that the PLA and PLA-PVP-I coatings both showed smooth surfaces without visible porosity, indicating proper melting and plastic deformation of PLA particles during the spraying process (Fig. 1c, d). The fractured surfaces of PLA and PLA-PVP-I coatings were some distinct

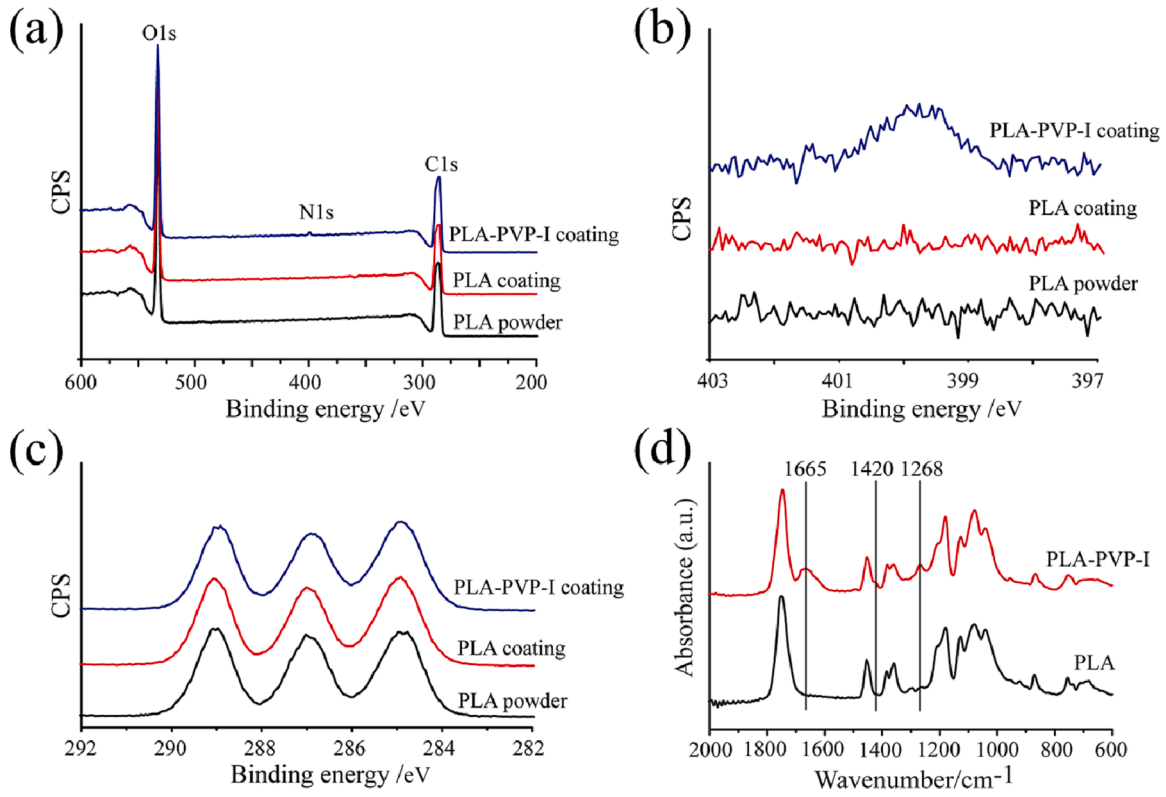

Fig. 2. XPS spectra of the powder and coatings (a) and high resolution XPS spectra of N1s (b) and C1s (c); (d) FT-IR spectra measurement.

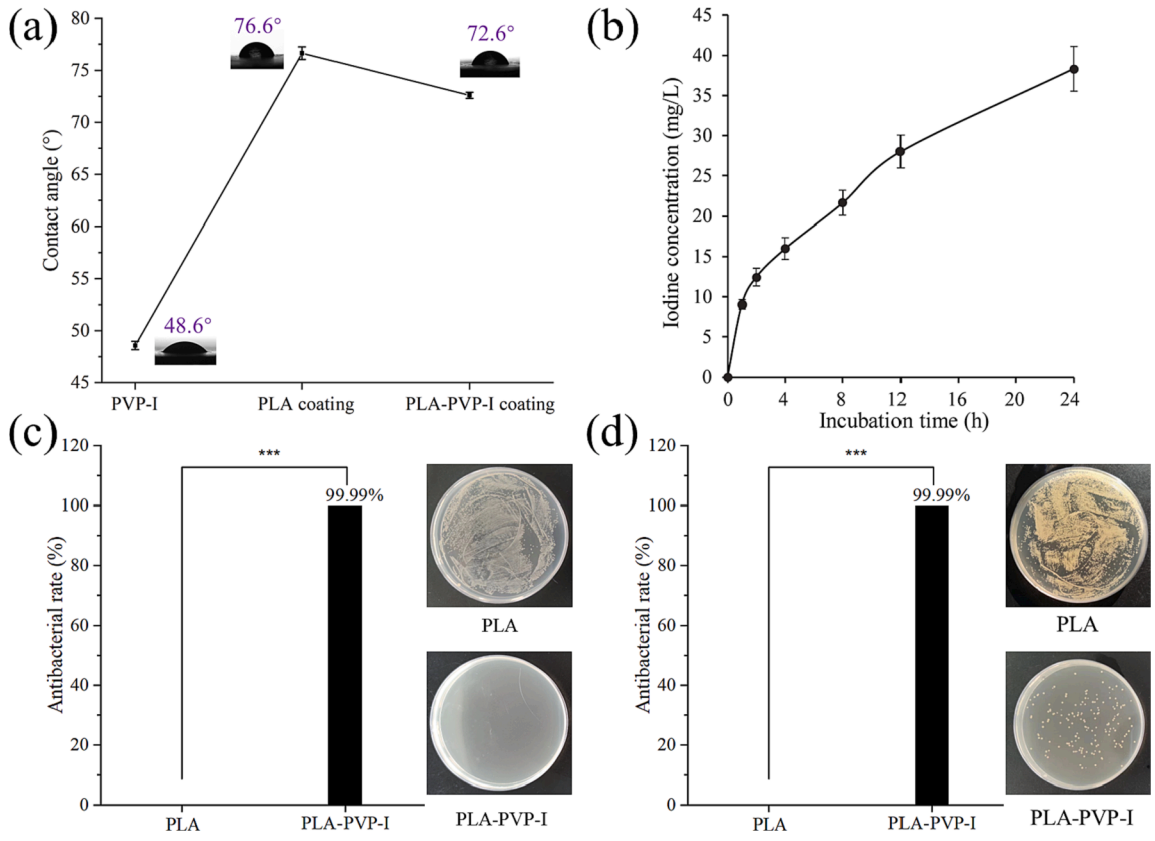

Fig. 3. (a) Contact angles of the PVP-I powder, the PLA and PLA-PVP-I coatings; (b) Cumulative release of iodine from the PLA-PVP-I coating *in vitro;* Antimicrobial activities of the PLA-PVP-I coatings against (c) *E. coli* and (d) *S. aureus* after 4 h contact time, ***$p < 0.001$.

river markings, and confirmed the inherent stiffness and brittle character of pristine PLA (Fig. 1e, f) [11]. EDS result shown that I peak confirmed the presence of PVP-I component, revealing that PVP-I particles are successfully loaded in the interior structure of composite coating.

XPS analysis of the PLA powder, PLA coating and PLA-PVP-I coating was shown in Fig. 2. Similar C1s and O1s peaks were observed for all three samples (Fig. 2a). The high resolution C1s spectra further showed characteristic peaks around 285, 287 and 289 eV for PLA powders, PLA and PLA-PVP-I coatings [12], indicating that the chemistry composition of PLA was well reserved during the flame spray process (Fig. 2c). Furthermore, a specific N1s peak around 400 eV was detected in both wide and high-resolution XPS spectra for the PLA-PVP-I coating, which corresponded to the N from the amide group in polyvinyl pyrrolidone (Fig. 2a-b). FT-IR analyses were conducted to further confirm the successful incorporation of PVP-I into the PLA coating (Fig. 2d). The characteristic peaks located at 1752 cm^{-1}, 1182 cm^{-1}, 1129 cm^{-1}, 1080 cm^{-1} represent the backbone ester group of PLA [13], and the addition of PVP-I did not trigger changes of these peaks. Three specific absorbance peaks at 1665 cm^{-1}, 1420 cm^{-1} and 1268 cm^{-1} were observed for the PLA-PVP-I coatings, which were attributed to the C═O stretching (amide I band), CH_2-C stretching and the C-N stretching in the pyrrolidone ring of PVP, respectively. They well corresponded to the three characteristic FT-IR absorbance peaks of standard PVP samples as previously reported [14].

The hydrophily of sample was assessed by the contact angle measurement. As shown in Fig. 3(a), PVP-I is quite hydrophilic with an average contact angle of 48.6°. The PLA coating shown an average contact angle of 76.6°, while that of the PLA-PVP-I coating slightly deceased to 72.6°, which might be due to the introduction of PVP-I component.

PVP-I is highly soluble in water and the hydrophily of the PLA-PVP-I composite coating would benefit the release of PVP-I after contact with physiological environment. The release of iodine from the PLA-PVP-I coatings in PBS solution was quantitatively determined (Fig. 3b). It is shown that the PLA-PVP-I coatings facilitated rapid release of iodine within hours and the release rate slowed down with incubation time.

Furthermore, *E. coli* and *S. aureus* bacterium were used to quantitatively determine the antibacterial properties of the PLA-PVP-I coatings (Fig. 3c, d). The results suggested that the viable colonies of both *E. coli* and *S. aureus* decreased sharply after inoculated with PLA-PVP-I coatings for 4 h. The relative viability of both *E. coli* and *S. aureus* was lower than 0.01%, which implied that the killing efficiency against them was over 99.99 %. Free molecular iodine (I_2) released from the PLA-PVP-I coatings are mainly responsible for the antibacterial activity.

4. Conclusions

Novel PLA-PVP-I coatings were fabricated by liquid flame spray and showed excellent antibacterial performance. PLA serves as the matrix to fix and release PVP-I for highly efficient antibacterial functions. The cost-effective fabrication technique to produce biodegradable polymer-based antibacterial coatings will shed light on the development of surface-functionalized biomedical materials for various applications.

CRediT authorship contribution statement

Yonghong Pan: Methodology, Investigation, Writing – original draft, Software. **Lei Ye:** Investigation. **Ping Zhou:** Software. **Xiaohua Feng:** Methodology, Investigation. **Yi Liu:** Writing – review & editing, Funding acquisition. **Botao Zhang:** Conceptualization, Writing – review & editing, Supervision, Funding acquisition. **Hua Li:** Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

The data that has been used is confidential.

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References

[1] C.E. Vantucci, H. Ahn, T. Fulton, M.L. Schenker, et al., Biomaterials 264 (2021), 120405, https://doi.org/10.1016/j.biomaterials.2020.120405.
[2] C. Offerhaus, M. Balke, J. Hente, M. Gehling, et al., Knee Surg. Sports Traumatol. Arthrosc. 27 (9) (2019) 3014–3021, https://doi.org/10.1007/s00167-018-5323-6.
[3] J.-A.-D. Olmo, L. Ruiz-Rubio, L. Pérez-Alvarez, V. Sáez-Martínez, et al., Coatings 10 (2020) 2, https://doi.org/10.3390/coatings10020139.
[4] D.A. Ertek, N.O. Sanli, Y.Z. Menceloglu, S. Avaz Seven, Eur. Polym. J. 185 (2023), 111804, https://doi.org/10.1016/j.eurpolymj.2022.111804.
[5] H. Xu, M. Shen, H. Shang, W. Xu, et al., Ind. Eng. Chem. Res. 60 (32) (2021) 12021–12031, https://doi.org/10.1021/acs.iecr.1c02165.
[6] M. Tang, K. Xu, H. Shang, X. Li, et al., Int. J. Biol. Macromol. 226 (2023) 1273–1283, https://doi.org/10.1016/j.ijbiomac.2022.11.240.
[7] H. Xu, L. Jiang, L. Ke, G. Zhu, et al., ACS Appl. Polym. Mater. 4 (12) (2022) 9231–9240, https://doi.org/10.1021/acsapm.2c01502.
[8] M. Răpă, A.C. Miteluț, E.E. Tănase, E. Grosu, et al., Compos. B Eng. 102 (2016) 112–121, https://doi.org/10.1016/j.compositesb.2016.07.016.
[9] K.O. Oduwole, A.A. Glynn, D.C. Molony, D. Murray, et al., J. Orthop. Res. 28 (9) (2010) 1252–1256, https://doi.org/10.1002/jor.21110.
[10] H. Chen, Y. Jin, L. Lei, X. Ding, et al., Appl. Surf. Sci. 587 (2022), https://doi.org/10.1016/j.apsusc.2022.152911.
[11] H. Gao, T. Qiang, Materials 10 (2017) 6, https://doi.org/10.3390/ma10060624.
[12] X.G. Zhao, K.J. Hwang, D. Lee, T. Kim, et al., Appl. Surf. Sci. 441 (2018) 381–387, https://doi.org/10.1016/j.apsusc.2018.01.257.
[13] L. Ke, H. Shang, M. Tang, X. Li, et al., Int. J. Biol. Macromol. 220 (2022) 827–836, https://doi.org/10.1016/j.ijbiomac.2022.08.114.
[14] J. Li, H. Pan, Q. Ye, C. Shi, et al., J. Drug Delivery Sci. Technol. 58 (2020), 101726, https://doi.org/10.1016/j.jddst.2020.101726.