Functionalization of polylactic acid thin films via polydopamine-assisted chelation of copper (II) ions for antibacterial applications

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Abstract. Polylactic acid (PLA) is a biodegradable polymer, which has been widely investigated for use in biomedical and packaging applications due to its excellent biodegradability, biocompatibility, non-toxicity, low cost, good stability, and thermal processability. In this work, PLA was functionalized to improve the membrane’s hydrophilicity and impart antimicrobial activity by simultaneously depositing polydopamine (PDA) and chelating Cu²⁺ metal ions on the membrane surface. Pristine PLA films were modified via one-pot dip coating method using dopamine-copper (II) solution at different coating times (6, 12, 24 h). FTIR analysis confirmed the deposition of PDA on the modified membranes (PLA/PDA/Cu) as indicated by the presence of catechol and amine moieties on the samples. TGA results revealed the degradation of the same functional groups on PLA/PDA/Cu. The hydrophilicity of PLA was significantly reduced upon coating with PDA as indicated by the decrease in the membrane’s contact angle from 96.5 ± 5.3° to 56.2 ± 4.7°. SEM images and EDS results clearly showed that copper particles were deposited on the PLA/PDA/Cu membranes (atomic % ~ up to 0.88) and coating with PDA did not alter the porous structure of the pristine PLA film. Results also demonstrated that the concentration of copper immobilized on the modified membranes increased with longer coating; thus, offering a way of tailoring the metal concentration on the membrane for its specific use. PLA/PDA/Cu membranes showed antibacterial property against the B. subtilis, which could be attributed to the chelation of Cu²⁺ ions with the catechol moiety of the PDA coating.

1. Introduction

One of the best-known biopolymers is polylactic acid (PLA), a biodegradable aliphatic polyester that can be derived from lactic acid and can be produced from fermentation of renewable sources. It has been widely investigated for practical medical applications—scaffolds in tissue engineering [1], surgical sutures and dressing materials [2], and wound healing dermal patch [3]—and as green alternative for food packaging applications [4]. Such considerable interest has been given to PLA and its copolymers because of their excellent biocompatibility and biodegradability. The biopolymer degrades, by random hydrolysis of its ester bonds, to form lactic acid or its naturally occurring metabolites that are normally present in the human body. In addition, it exhibits non-toxicity, low cost, stability, and thermal processability [5]. But despite its many advantages, PLA also exhibit several
limitations including high hydrophobicity and lack of antibacterial activity; hence, it requires some modifications to increase its desirability and further its use in certain applications.

One of the promising approaches to modify and impart specific functions to polymeric materials including PLA, is the use of mussel-inspired polydopamine (PDA) coating [1,6,7]. Marine mussels are well known to adhere on different substrates under moist conditions. The adhesion is due to *Mytilus edulis* foot protein 5 (Mefp-5), which has the reactive catechol-containing compound 3,4-dihydroxyphenyl-L-alanine (DOPA) and lysine, distributed at the interface between the protein and the substrate. The ortho-dihydroxyphenyl group of the catechol is responsible for the excellent adhesive property of the organism to a wide variety of organic and inorganic surfaces [8]. Lee and co-workers [9] identified dopamine (DA)—a small-molecule compound that contains both catechol (DOPA) and amine (lysine) functional groups—as a simple structural mimic of Mefp-5, and showed that such is a powerful building block for the spontaneous deposition of thin polymer films on virtually any bulk material surface and that the films are adapted for a wide variety of functional uses. Inspired by this phenomenon, they introduced a simple method to form multifunctional polymer coatings by simple immersion of a material in an aqueous solution of DA under alkaline conditions where the latter undergo self-polymerization to form PDA. The most interesting property of the PDA coating is its adhesive function such that it can strongly adhere to a variety of materials including metals, oxides, semiconductors, polymers, and ceramics [9]. It also promotes cell adhesion and immobilization of bioactive molecules and is amenable to post-functionalization via catechol chemistry [8]. Another advantage of PDA is it is non-toxic and produces no harmful by-products during mild formation process. Nonetheless, despite the excellent adhesive property and biocompatibility of PDA, it has been reported that its antibacterial effect—an important requirement for medical biopolymers—is only moderate [10–12].

In this work, Cu (II) metal ions were used to impart antibacterial function to PLA films with the use of PDA surface coating. Metal nanoparticles are well known to have antibacterial properties and have been extensively studied for the development of antibacterial surface coatings. In particular, silver nanoparticles (AgNPs) have been found highly effective in imparting antibacterial function when utilized in titanium implants, medical devices, and organic polymers [13–16]. However, its use may be limited due to its high cost and relative toxicity. Another metal with excellent antibacterial property, yet less expensive than silver, is copper. It has been reported copper has less toxicity compared to other heavy metals, including silver [16,17]. Several studies suggest that copper is a promising metal ion for antibacterial application not only because of its lower toxicity but also its higher cytocompatibility. Xing et al. [18] successfully constructed an antimicrobial polyethersulfone (PES) membrane via PDA-assisted immobilization of copper ions on the polymer surface. They showed that the prepared PES-PDA-Cu membranes exhibited highly effective antibacterial activity with a relatively safe release amount of copper ions. Also, it has been demonstrated that upon incorporation in titania (TiO₂) coating, Cu²⁺ would have the best compromise between antibacterial effectiveness and cytotoxicity as compared to Ag⁺, Hg²⁺, Al³⁺, Co²⁺, and Zn²⁺ ions [19]. In addition, copper is naturally present in the body and it undergoes metabolization, while silver does not which results in increased body silver serum level [17,20]. Although copper is a well-recognized antibacterial metal, its use as an antibacterial agent on biodegradable PLA systems has not yet been fully investigated to date. Thus, this study aimed to modify the surface of PLA thin film by coating with PDA and impart antibacterial function through deposition of Cu (II) metal ions on the polymer surface. It also provided an extensive characterization of the functionalized PLA/PDA/Cu membrane composite.

2. Experimental Section

2.1. Materials

Polyactic acid (PLA polymer 6202D, pellets, MW = 140 kDa; 98 % L-Lactide, 2 % D-Lactide) was obtained from Natureworks. N-methyl-2-pyrrolidone (NMP, ≥ 99.8 %) was supplied by RCI Labscan Ltd. while dopamine hydrochloride (3-hydroxytyramine hydrochloride, 98 %) and tris(2-amino-2-
hydroxymethyl-propane-1,3-diol) (Tris-HCl, 99%) were purchased from Sigma Aldrich (USA). Copper sulfate pentahydrate and hydrochloric acid was obtained from Merck KGaA (Germany). All chemicals were used as received. Type I deionized water was used in the preparation of solutions.

2.2. Method
Polylactic acid (PLA) films were prepared via liquid induced phase separation (LIPS) technique. First, PLA polymer solution was prepared by dissolving a specific amount of PLA (13 wt. %) pellets in NMP while stirring at 60 °C for at least 6 hours. The solution was then cast on a glass plate using a casting knife, exposed to air for 10 s, and immersed into a nonsolvent (water) bath at room temperature. Both plate and knife were heated in an oven at 60 °C before use. The membrane was allowed to form, then soaked into and rinsed thoroughly with deionized water several times to remove the remaining solvent (NMP). Finally, the membrane was dried in air and stored at room temperature.

The surface of prepared PLA film was modified using a one-pot dip coating procedure, according to method proposed by Liu et al. [21]. Copper sulfate solution (100mM) was prepared by dissolving CuSO₄·5H₂O in Tris-HCl buffer solution (50 mM, pH = 8.5). The pH of the solution was further adjusted to 4.5 by adding a small amount of 1 M HCl. The pH was measured using a pH meter (Sartorius PB-10). The coating solution (dopamine-Cu²⁺) was then prepared by adding 100 mg of dopamine HCl to 50 mL (2 mg dopamine/mL) of the prepared CuSO₄ solutions. The PLA membrane (2 × 3 in) was soaked in the freshly prepared dopamine-Cu²⁺ solution in a plastic pan with mild heating at 30 °C using an incubator shaker (Fine PCR BAE07-H300) for 6 h. The solution was kept agitated at 50 rpm to minimize aggregation of PDA and Cu²⁺ particles on the surface of the membrane. After which, the modified PLA membrane was gently rinsed with deionized water several times to wash loosely bounded particles from the membrane surface before drying in air. The dried membrane composite (PLA-/PDA/Cu) was stored at room temperature until further characterization. The experiment was done at varying soaking times (6, 12 and 24 h) to investigate the effect of coating time on the deposition of PDA and Cu²⁺ on the PLA membrane surface. The samples were identified as PLA-/PDA/Cu-6h, PLA-/PDA/Cu-12h, and PLA-/PDA/Cu-24h, respectively.

A Fourier transform infrared spectroscopy (FTIR, Perkin Elmer) was performed in attenuated total reflection (ATR) mode, in the wavenumber range 4000 – 400 cm⁻¹, to confirm the deposition of PDA on PLA membrane surface. The thermogravimetric analysis (TGA) was done using a simultaneous thermogravimetric analyser (DSC/TGA, Hitachi NEXSTA STA 200RV) using nitrogen as purge gas. The sample (approximately 5 mg) was heated from 25 to 500 °C at a heating rate of 10 °C/min. Furthermore, the hydrophilicity of PLA and modified membrane samples was determined using an optical tensiometer (Theta Lite). The morphology of each membrane sample was characterized using a scanning electron microscope (SEM, Hitachi SU3500) using an accelerating voltage of 15 kV. The equipment was coupled with an energy dispersive X-ray spectrocope (EDS, Bruker X Flash 6/60), which was used to determine the concentration and distribution of copper on the surface of the membrane by area and spot scanning.

Antibacterial function of the prepared PLA and modified membrane samples was tested against the gram-positive bacteria Bacillus subtilis using the disc diffusion method. The bacteria were spread in a sterilized agar plate using metal loop spreader, then the membrane samples were placed atop of it. One-inch discs of membrane samples, which were cut into quarters, were used in the experiment. The plate was then left to incubate in an incubator oven at 37 °C for 24 h with monitoring at (3, 6, 12, 24) h. Tests were done for samples coated in different concentrations of dopamine-CuSO₄ solutions (50, 100, 150 mM).

3. Results and Discussion

3.1. FTIR Analysis
FTIR spectra were determined for pristine PLA and PLA/PDA/Cu films to key out the functional groups in the fabricated polymer and confirm the deposition of polydopamine on the PLA surface.
FTIR results for pristine PLA and PLA/PDA/Cu composites are shown in figure 1. Characteristic peaks at 2995 and 2946 cm\(^{-1}\) were observed in all samples, which belong to the symmetric and asymmetric C–H stretching of \(-\text{CH}_3\) in PLA, respectively. PLA also showed stretching frequencies for C=O at 1751 cm\(^{-1}\) and for C–O at 1182 and 1084 cm\(^{-1}\). Bands identified at 1452 and 1359 cm\(^{-1}\) can be assigned to the bending of \(-\text{CH}_3\) groups in PLA. Such observations exhibit close similarity with those reported in the literature [22, 23]. The identified peaks in pristine PLA were also present in the spectra of PLA/PDA/Cu composites. For the said composites, broad peaks were observed at 3198 cm\(^{-1}\) and 3228 cm\(^{-1}\) for PLA/PDA/Cu-6h and PLA/PDA/Cu-24h, respectively. These absorbances correspond to both the catechol O–H and N–H stretching vibrations present in the PDA layer. Furthermore, some new absorption peaks were observed at 1617 and 1509 cm\(^{-1}\). The peaks at 1617 cm\(^{-1}\) can be attributed to the overlapping of the C=C stretching vibration in the aromatic ring and N–H bending vibration in PDA. These can be identified with the FTIR spectra of PDA reported by Zhao \textit{et al.} [24] as shown in figure 2a. The slight shift in the bending bands from 1623 (for PDA) to 1617 cm\(^{-1}\) in the case of the PLA/PDA/Cu composites can be due to the molecular interactions of the amine group of dopamine on the surface of the PLA. On the other hand, the peaks at 1509 cm\(^{-1}\) can be ascribed to the N–H shearing vibration of PDA. Such results are consistent with those reported by Liu \textit{et al.} [21] and provide strong evidences for the successful coating of PDA on the PLA substrate.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure1.png}
\caption{FTIR spectra of (a) pristine PLA; (b) PLA/PDA/Cu-6h; (c) PLA/PDA/Cu-24h.}
\end{figure}

It can be hypothesized that PDA adsorbed on PLA since catechol—one of the main functional groups in PDA—interact effectively with almost any kind of surface. In this study, the binding of PDA on PLA can be attributed partially to hydrogen bonding between the hydroxyl and/or amine groups in the catecholamine and the polar carbonyl and hydroxyl groups in the PLA substrate. Such nature of interaction was also reported for some organic and polymeric substrates bearing polar groups including poly(allylamine), polyethylene glycol (PEG) and polyethyleneimine (PEI). However, it has to be noted that the contributions from covalent bonding cannot be completely discounted [25, 26]. Zhao \textit{et al.} [24] reported similar observations for PDA deposited on PLA pellets where N–H/O–H stretching bands were identified between 3680 and 3050 cm\(^{-1}\) (figure 2b). It is also worth noting that the spectra of PLA/PDA/Cu-6h and PLA/PDA/Cu-24h films were greatly similar. However, the intensity of the peak at 3223 cm\(^{-1}\) (PLA/PDA/Cu-24h) significantly increased compared with that at 3198 cm\(^{-1}\).
(PLA/PDA/Cu-6h) suggesting that the amount of polydopamine deposited on the PLA surface increased with longer coating time.

Figure 2. FTIR spectra of (a) PDA [24]; (b) PLA/PDA [24]; (c) PLA/PDA/Cu-24h (this work).

3.2. Contact Angle Measurements
To further validate the deposition of PDA on the substrate, static contact angle measurements were performed on the membrane surfaces. As shown in figure 3, the water contact angle of pristine PLA was measured to be 96.5 ± 5.3° indicating the inherent hydrophobicity of the membrane. After coating the PLA sample with PDA and copper for 24 h, the water contact angle decreased remarkably to 56.2 ± 4.7°. It is to be noted that the reported the contact angle of PDA on glass substrate was 27.8 ± 4.3° indicating that it is highly hydrophilic [24]. Hence, the relative hydrophilicity of PLA/PDA/Cu-24h membrane sample was a good indication that the PLA membrane surface was coated with PDA. Such improvement of the hydrophilicity of the membrane surface was expected because of the presence of hydrophilic hydroxyl and amino groups in the PDA molecule and would be advantageous in promoting cell adhesion [21].

Figure 3. Water contact angle of surface: (a) PLA film; (b) PLA/PDA/Cu-24h; (c) PDA [24].
3.3. **TGA Analysis**

Figure 4 shows the TGA curves for pristine PLA and coated PLA/PDA/Cu-24h from this work and for pure DA obtained by De Guzman and co-workers [27]. PLA showed a one-step degradation process similar to that reported by Dai et al. [28] where the polymer started to degrade at 250 °C until 360 °C indicating the decomposition of oxygen-containing functional groups [29]. After heating the sample to about 500 °C, 1.37 % residual remained, which could be expected as PLA completely degrades above 900 °C [30]. De Guzman et al. [27] reported the decomposition of DA, starting at 180 °C to 220 °C, which was attributed to the evaporation of adsorb water in the monomer. Continuous decomposition occurred at 210 °C to 325 °C, which is due to the degradation of the catechol moiety while the amine functional groups decomposed from 325 °C to 425 °C (third decomposition). It can be observed that the thermal decomposition behaviour of the coated PLA/PDA/Cu-24h sample was similar with that of PLA. However, the initial degradation temperature of the coated sample was lower than that of the pristine polymer. As shown, the first observable weight loss of about 3.14 % occurred at 50 °C to 200 °C indicating the removal of adsorb water on the sample. Such result can be attributed to the low starting degradation temperature of PDA layer deposited on the PLA substrate. Further weight loss to up to 300 °C corresponded to the decomaposition of the hydroxyl group in PDA. Above 300 °C, the simultaneous degradation of the amine moiety in PDA (at 300 °C to 335 °C) and oxygen-containing functional groups in PLA may have caused the shift in the degradation curve of PLA. It can also be noted that the coated PLA/PDA/Cu-24h exhibited a slower degradation compared to pristine PLA, which indicated the relative stability of the coated sample at higher temperatures. Such could be attributed to the presence of copper particles on the sample surface, which may have prevented the burning. This finding was further supported by the increased residual weight obtained for PLA/PDA/Cu-24h of approximately 5.90 %.

![Figure 4. TGA curves for PLA and PLA/PDA/Cu-24h films (this work), and dopamine (DA) nanoparticle [27].](image)

3.4. **Morphology**

Scanning electron microscopy (SEM) was used to observe the morphologies of the membrane samples before and after deposition of PDA and copper. Figure 5a shows the SEM image of pristine PLA. It was observed that the membrane was highly porous and characterized by a microporous structure with pore sizes ranging from 0.8 to 2.5 μm. Figure 5 also shows a comparison of the pristine PLA sample with the coated PLA/PDA/Cu composites. It is important to note that the even after deposition of PDA on the substrate’s surface, the highly porous structure of PLA was preserved. This attribute is greatly advantageous in the utilization of the biopolymer in numerous applications. Moreover, the composites were characterized by the presence of microcracks on the sample surfaces, which could be identified as the PDA film coated on the substrate surface. This observation can be more clearly seen in figure 6.
with the SEM images of PLA/PDA/Cu-6h and PLA/PDA/Cu-24h. The occurrence of such microsized cracks was also observed by Zhang et al. [31] on PDA films deposited on polydimethylsiloxane (PDMS), and was attributed to the difference in elastic modulus between the rigid PDA film and its soft substrate. Drying and storage of the membrane samples in air resulted in the formation of these microcracks. The cracking of PDA films on poly(L-lactide) and silicon oxide substrates were also reported in other studies [32, 33]. Furthermore, the microcracks found in PLA/PDA/Cu-24h were more prominent than those in PLA/PDA/Cu-6h sample indicating the formation of a thicker layer of PDA on the substrate that was coated for 24 h. This finding supports the results obtained from the FTIR analysis where the concentration of amine groups (or PDA) on the sample increased with longer coating time.

Figure 5. SEM images of (a) pristine PLA; (b) PLA/PDA/Cu-6h; (c) PLA/PDA/Cu-12h; (d) PLA/PDA/Cu-24h.

Figure 6. SEM images of (a) PLA/PDA/Cu-6h and (b) PLA/PDA/Cu-24h.

SEM images in figures 5 and 6 also display the presence of copper particles (light points) deposited on the surface of the coated samples (PLA/PDA/Cu-6h, PLA/PDA/Cu-12h and PLA/PDA/Cu-24h). Such finding was confirmed by an EDS point analysis on the particles, which revealed that they were mainly consisted of copper. According to Liu et al. [21], who characterized the valence states of copper present during the polymerization of dopamine in the presence of CuSO₄ in solution, copper ions were present as Cu⁺ and Cu²⁺. As it is well known that PDA binds with metals via chelation, it
can be said that the immobilization of copper on the PDA coating can be attributed to the chelation of Cu^{2+} or Cu^{+} ions. In particular, copper ions are proposed to exhibit interaction with the catechol moiety of the catecholamine [21, 32, 34]. It could also be noted that the hydrophilicity of PDA may have played a role in the deposition of the metal ions. It is worth noting that copper played an important role in the formation of PDA layer on the coated membrane because the polymerization of dopamine was initiated by Cu^{2+} metal ion in the solution. Although dopamine is known to self-polymerize only under alkaline environment, it has been reported in recent works [21, 32] that Cu^{2+}, in the presence of air, initiates the polymerization of dopamine in acidic conditions (pH = 4.5). Such can be indicated by the rapid color change of the coating solution from clear to dark brown observed in this work. Moreover, formation of dopamine-Cu^{2+}-oxygen complex may have possibly enhanced the rate of polymerization of dopamine. Although the exact structure of PDA has not yet been fully elucidated, literature suggests that the configuration of PDA becomes crosslinked at the phenyl sites upon oxidation of dopamine [35]. Nonetheless, since the exact structure of PDA remains under debate further investigations would be necessary to fully understand and explain the mechanism of reaction of Cu^{2+} in the polymerization of dopamine. It is clearly shown in figure 6 that copper particles were distributed on sample surfaces where a more even distribution obtained in PLA/PDA/Cu-24h. The particle sizes ranged from 300 – 900 nm. However, it seemed that agglomeration of the particles during the coating process was inevitable that some form into bigger clusters (up to ~1.5 μm). Nevertheless, the results evidently show that the PLA substrate was successfully coated with a layer of PDA and copper.

3.5. EDS Analysis
Energy-dispersive X-ray spectroscopy (EDS) area scanning was done to estimate the distribution and atomic percentage of copper for different coating times and concentrations of CuSO_{4} in the soaking solution. Table 1 shows the EDS analyses of PLA/PDA/Cu samples for different coating times. Results indicated that a significant amount of Cu element was present on the sample surface with increasing atomic percentage as coating time in the dopamine-Cu^{2+} solution increased. A similar observation can be seen for the atomic percentage of nitrogen element. Furthermore, a high percentage of elemental nitrogen gives a clear indication that the PDA was abundantly present on the coated membrane. These results suggest that the concentration of copper immobilized on the modified membrane may be controlled for specific applications by adjusting the coating time. Such will offer a way of tailoring the concentration of copper in the membrane to levels that would provide antibacterial effect and pose limited toxicity risks when leached. Although leaching of copper was not addressed in the present work, a comparison with results obtained by Xing et al. [18] for PES-PDA-Cu membrane revealed that given the amounts of copper immobilized in the studied membrane, possible leaching of copper would be below the maximum contaminant limit in the human body (below 1 ppm).

Table 1. Energy-dispersive X-ray spectroscopy (EDS) analysis of PLA/PDA/Cu samples for different coating times.

| Time (h) | Atom (%) | C | O | N | Cu |
|---------|----------|---|---|---|----|
| 6       |          | 41.00 | 50.50 | 7.96 | 0.53 |
| 12      |          | 41.42 | 49.48 | 8.36 | 0.75 |
| 24      |          | 39.68 | 49.79 | 9.68 | 0.86 |

3.6. Antibacterial Test
Pristine PLA and coated PLA/PDA/Cu membrane samples were subjected to antimicrobial test against the gram-negative bacteria *Bacillus subtilis* at different incubation times. The results are summarized in table 2. Results showed that bacterial growth started on the edges of pristine PLA as early as 3 h of incubation. This was the case for the coated PLA/PDA/Cu50 sample after 6 h incubation time, and for the modified PLA/PDA/Cu100 and PLA/PDA/Cu150 only after 12 h. More importantly, no visible bacterial growth was observed on the surface of all modified samples even after 24 h, while significant
growth was seen covering the entire surface of the control sample (PLA) after 12 h. As indicated in table 2, for samples PLA/PDA/Cu50, PLA/PDA/Cu100 and PLA/PDA/Cu150, bacterial growth was absent in the entire duration of the test on the whole sample surface where PDA and Cu$^{2+}$ ions were available. These results suggest that the coated samples exhibit antimicrobial protection against B. subtilis. The antimicrobial property of the studied PLA/PDA/Cu membrane composites may be attributed to the presence of copper ions, mainly Cu$^{2+}$, on the samples’ surfaces. It is known that Cu$^{2+}$ has strong antimicrobial activity, as it is capable of penetrating bacterial cell walls causing oxidation of the core cell, which eventually leads to death [17, 19, 36–37]. In this study, it was evident that copper was immobilized on the surface of all modified membrane samples, and their antimicrobial effect on a representative bacterial strain (B. subtilis) was successfully demonstrated. These results would suggest that the prepared PLA/PDA/Cu membrane could be effective in preventing bacterial infection.

Table 2. Antibacterial test results for coated PLA/PDA/Cu membrane samples vs. Bacillus subtilis at different incubation times.

| Sample            | Time (h) |
|-------------------|----------|
|                   | 3    | 6    | 12   | 24   |
| PLA               | +    | ++   | +++  | +++  |
| PLA/PDA/Cu50      | −    | +    | ++   | ++   |
| PLA/PDA/Cu100     | −    | −    | ++   | ++   |
| PLA/PDA/Cu150     | −    | −    | ++   | ++   |

Legend: − No visible growth along sample edges
+ Visible growth along sample edges
++ Visible growth along sample edges but none on sample surface
+++ Visible growth along sample edges and surface

4. Conclusions
PLA films were successfully functionalized by simultaneous deposition of PDA membrane surface and chelation of Cu$^{2+}$ metal ions on the PDA coating using a one-pot dipping method. FTIR and TGA results indicated that the PLA surface was coated with PDA as confirmed by the presence and degradation of $-\text{OH}$ and $-\text{NH}$ functionalities. The modified membrane was shown to be hydrophilic by contact angle measurements, while SEM-EDS analyses provided clear evidence of copper particles deposited on the membrane surface. The fabricated PLA/PDA/Cu membrane showed decent antibacterial property against the B. subtilis due to Cu$^{2+}$ ions chelated on the membrane surface. Thus, the prepared membrane can be potentially be used for antimicrobial applications.

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