Polycaprolactone/polyvinyl pyrrolidone nanofibers developed by solution blow spinning for encapsulation of chlorogenic acid

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Abstract

Study on the application of nanofibers in food active packaging has been a research hotspot in recent years. In this work, the solution blow spinning (SBS) was applied to rapidly fabricate the polycaprolactone (PCL), polyvinyl pyrrolidone (PVP), and PCL/PVP nanofibrous films to encapsulate chlorogenic acid (CGA). All the films showed uniform and smooth nanofibers, and the FTIR and XRD proved the success of mixed spinning of PCL and PVP. With the increase of PVP content, the thermal stability of the PCL/PVP nanofibrous films improved. The PCL/PVP (4:1) film possessed better mechanical properties than PCL and PVP films because of the stronger fiber-fiber interactions. The addition of PCL endowed the hydrophobic surfaces to the PCL/PVP films, and the PCL/PVP films had better water vapor barrier ability. The PCL/PVP (4:1) film exhibited the best long-term continuous release of CGA during 72 h. The PVP nanofibrous film exhibited no inhibition against S. aureus and E. coli due to the low encapsulation efficiency, but the PCL and PCL/PVP films exhibited good antimicrobial activity. The above results suggested that the nanofibrous films developed by SBS possessed the promising prospects in food packaging.

Keywords

Solution blow spinning; polycaprolactone; polyvinyl pyrrolidone; chlorogenic acid; long-term continuous release
1. Introduction

Solution blow spinning (SBS) is an emerging technology for the production of polymeric nanofiber films with high specific surface area (Shen et al., 2021a). An SBS device generally consist of four components, including an air pump, a syringe pump, concentric nozzles and a collector; in the process of fabrication, the high-speed airflow in the outer nozzle is capable of elongating the polymer solution in the inner nozzle into fine fibers (Benavides et al., 2012; Yang et al., 2021). SBS has a variety of applications, including impurity filtration, sensors, the medical industry and wearable electronic devices (Dias et al., 2020; Shen et al., 2021a). However, in the field of food packaging, where nanofibers also have a broad application prospect, the study of spinning methods for the preparation of nanofibers is mainly based on electrospinning, and there are only a few studies on SBS (Duan et al., 2021; Guo et al., 2022; Ni et al., 2021; Wang et al., 2019; Yang et al., 2021; Zhang et al., 2020). Compared to electrospinning technology, SBS has a number of advantages, such as a short preparation time, wide range of materials, high usage value and relatively higher safety with no high voltage (Gao et al., 2021). Particularly, some prior studies have shown that SBS could be more efficient in fiber production than electrospinning, with production rates up to 3-30 times higher (Sett et al., 2016; Tandon et al., 2019). This makes the SBS technology promising for the rapid fabrication of nanofiber films for food packaging materials.

Polyvinyl pyrrolidone (PVP) is a hygroscopic synthetic polymer obtained from the monomer N-vinylpyrrolidone, with excellent biocompatibility and non-toxicity, and has been widely applied in the food, medical and pharmaceutical areas (Bandyopadhyay et al., 2019; Haaf et al., 1985; Rahmani et al., 2021a; Sandoval-Herrera et al., 2021). Nevertheless, given the high hydrophilic nature and its inferior mechanical properties, polyvinyl pyrrolidone nanofibers usually need to be modified using other synthetic polymers. For this reason,
synthetic polymers such as poly(vinyl alcohol) (PVA), poly(glycolic acid) (PLA) and poly(caprolactone) (PCL) have been investigated for the production of polymer composites with better properties (Li et al., 2014; Rahmani et al., 2021b; Zou et al., 2020).

PCL is a synthetic hydrophobic polymer, with superior biocompatibility and biodegradability, and has been employed extensively in food and biomedical fields (Gutiérrez et al., 2021; Martins et al., 2018). As reported in previous studies, PCL has been successfully used to modify PVP and use it as scaffolds for bone regeneration (Pranav Kumar Shadamarshan et al., 2018; Smaida et al., 2020). However, there has been little research on the use of SBS technology to develop PCL/PVP fiber films and use them for the aim of preparing antibacterial packaging.

Active substances are often encapsulated in materials for active packaging. Chlorogenic acid (CGA) is an ester formed from caffeic acid and quinic acid, which is present in fruits and vegetables. It has been shown that as a natural bioactive substance of plant origin, CGA can be added to packaging materials to extend the shelf life of foods as it possesses exceptional antibacterial and antioxidant performances (Fu et al., 2017; Shao et al., 2014).

In this study, SBS was adopted to produce CGA/PCL/PVP composite films to meet the necessity of rapid preparation of food packaging materials. The possibility of promoting the overall performance of PVP in the aspects of mechanical strength, solubility resistance and controlled release by using PCL as a modifier was evaluated. The micromorphology, molecular interaction, crystallinity, thermal properties, mechanical performance, water affinity and water vapor permeability (WVP) of the PVP, PCL/PVP and PCL films were characterized. Controlled release performance and antibacterial performance of the CGA/PVP, CGA/PCL/PVP and CGA/PCL films were also investigated.
2. Materials and methods

2.1. Chemicals

2,2,2-Trifluoroethanol (TFEA, $M_w = 100.04$ Da) and PBS buffer (50 mmol/L, pH 7.4) were obtained from Macklin Co., Ltd. (Shanghai, China). Polycaprolactone (PCL, $M_w = 80$ kDa, CAS: 24980-41-4) was purchased from Sigma-Aldrich Co., Ltd. (Shanghai, China). Anhydrous ethanol was obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Polyvinyl pyrrolidone (PVP, $M_w = 40$ kDa, CAS: 9003-39-8) was purchased from NantongFeiy Biological Technology Co., Ltd. (Nantong, China). Chlorogenic acid (CGA, $M_w = 354.31$ Da, CAS: 327-97-9) was supplied by Nanjing Herbal Source Biotechnology Co. Ltd. (Nanjing, China).

2.2. Microorganisms

The strains of Staphylococcus aureus (ATCC 6538) and Escherichia coli (ATCC 25922) were cultured on the Luria-Bertani medium (LB medium, Shanghai Bioresource Collection Center, China), and preserved in the Fruit Science Institute, Zhejiang University.

2.3. Preparation of spinning solution

The PCL solution was done by dissolving 1.44 g PCL (12%, w/v) in 12 mL 2,2,2-Trifluoroethanol. The PVP solution was obtained by dissolving 4.2 g PVP (35%, w/v) in 12 mL anhydrous ethanol (35%, w/v). The PCL/PVP solutions were done by dissolving 1.44 g PCL/PVP (12%, w/v) in 12 mL 2,2,2-Trifluoroethanol/ anhydrous ethanol, in which the weight ratios of PCL/PVP and the volume ratios of 2,2,2-Trifluoroethanol/ anhydrous ethanol were set at 2:1, 3:1, and 4:1, respectively. The 0.72 g CGA (6%, w/v) was added to each of these polymer solutions, obtaining CGA-loaded spinning solutions.
2.4. SBS process

Nanofibrous films were fabricated by SBS equipment (JNS-SBS-01, Nanjing Janus New Materials Co., Ltd., Nanjing, China). The prepared solution was added to a 20 ml syringe and the feed rate was set to 4 ml/hour. The air pressure was set to 0.100 MPa and the distance between the needle and the collector was 20 cm. Nanofilm preparation was performed at 25 °C and relative humidity (RH) of about 50%.

2.5. Fiber morphology analysis

FE-SEM (GeminiSEM 300, ZEISS, German) was used to observe the nanofiber morphology (Deng et al., 2019). Before the observation, the nanofibrous films were sputtered with gold. Nano Measurer 1.2 was used to obtain the average diameter by randomly measuring 100 fibers per SEM image.

2.6. Fourier transform infrared spectroscopy (FTIR) analysis

FTIR was performed using the KBr pellet method to determine the interactions between the components by a Nicolet iS50FT-IR instrument (Thermo Nicolet Ltd., USA). The wavenumber range was 4000-400 cm\(^{-1}\) and an average of 32 scans at 4 cm\(^{-1}\) were performed before baseline correction and smoothing (Lin et al., 2020; Sow and Yang, 2015; Yang et al., 2018).

2.7. X-ray diffraction (XRD) analysis

XRD was used to observe the crystal structures of the nanofibrous films (Zou et al., 2020). An Bruker D8 Advance (Bruker Co., German) was operated at 40 kV and 35 mA. The diffraction range was 5°–85° (2θ) and the scanning rate was 2° min\(^{-1}\).
2.8. Thermal analysis

TGA was performed using a Mettler Toledo STARRe System TGA2 (Mettler Toledo Crop., Switzerland) with a heating range of 50 to 600 °C (Zou et al., 2020). DSC was performed using a Mettler Toledo STARRe System DSC3 instrument (Mettler Toledo Crop., Switzerland) with a heating range of 20 to 200 °C (Yang et al., 2021). The heating rate of TGA and DSC was 10 °C min⁻¹.

2.9. Mechanical strength analysis

The mechanical strength of the nanofiberous films was measured by a mechanical test apparatus (Instron 5944, USA) (Shen et al., 2021a). The testing was performed with a 10 N loadcell, and a stretching rate was set to 1 mm min⁻¹. All samples were cut into strips (approximately 40 mm × 10 mm) with a thickness of 0.1 mm.

2.10. Water contact angle (WCA) analysis

WCA of nanofibrous films was measured using the sessile drop method by a contact angle goniometer (OCA20, Data Physics Co., Ltd., Germany). The droplet of distilled water (3.5 µL) was deposited on the surface of nanofibrous films. The WCA was determined by the angles of the left and right side of the water droplet. The water droplet need 3 s to reach steady state, and the angles at 0 s and 3 s were both observed and recorded. The values of WCA were calculated from five different positions on the film surface (Hasanpour Ardekani-Zadeh and Hosseini, 2019).

2.11. WVP analysis

The WVP values was calculated by using the ASTM E96 gravimetric method. The film was fixed on top of a permeation cup loaded with distilled water, and the cup kept in a desiccator containing dry silica gel. After reaching a steady state (approximately 1 h), the
permeation cups were weighed every 12 hours for three days. The WVP was obtained according to the following equation:

$$\text{WVP} = \frac{\Delta M \times d}{\Delta t \times \Delta p \times A}$$

where $\Delta M/\Delta t$ is the weight of water loss per unit time (g h$^{-1}$), $A$ is the area of the film exposed to moisture (m$^2$), $d$ is the film thickness (mm), and $\Delta p$ (3.1671 kPa at 25 °C) is the water vapor pressure difference crossing the film.

2.12. Encapsulation efficiency and in vitro release of CGA

The nanofibrous film (10 mg) was added into 10 mL anhydrous ethanol. After magnetic stirring at 200 rpm for 12 h, the concentration of CGA was measured by using a microplate reader (Synergy H1, BioTek) at 357 nm. The encapsulation efficiency was calculated by the following formula (Huang et al., 2020):

$$\text{Encapsulation efficiency (\%)} = \frac{M_i}{M_n} \times 100\%$$

where $M_i$ is the actual amount of CGA, $M_n$ is the theoretical amount. The CGA contents were calculated by a regression equation ($y = 0.0001x - 3 \times 10^{-6}$, $R^2 = 0.999$). Moreover, overfitting was analysed using AIC values: $\text{AIC} = n \ln(\text{SSE}) + 2p$, where $n$ represents the used data point number, SSE is the sum of squared estimates of error and $p$ is the number of the parameter used (Zhao et al., 2019).

The films (10 mg) were added to a vial containing 10 mL PBS buffer. The vials were left to stand at room temperature away from light. 200 µL supernatant was aspirated at intervals and the absorbance of the released CGA was measured at 357 nm by using the microplate reader. The volume in the vial was maintained at 10 mL by rapidly adding new PBS buffer after aspirating the supernatant for each measurement. The content of the released CGA was calculated by the following formula:
CGA release (%) = \frac{c_n \times V_0}{M_0} \tag{3}

where \( V_0 \) is the 10 mL PBS buffer system, \( M_0 \) is the actual total mass of CGA in the film. The CGA contents were calculated by a regression equation \( y = 0.0001x + 6 \times 10^{-7}, \ R^2 = 0.999 \).

Moreover, overfitting was analysed using AIC values: \( \text{AIC} = n \ln(\text{SSE}) + 2p \), where \( n \) represents the used data point number, \( \text{SSE} \) is the sum of squared estimates of error and \( p \) is the number of the parameter used (Chen et al., 2022).

The Korsmeyer-Peppas formula was used to analyze the results of the CGA in vitro release.

\[ R_t = k t^n \tag{4} \]

where \( R_t \) is the CGA release rate at time \( t \), \( n \) is the release exponent and \( k \) is the characteristic kinetics constant.

2.13. Antimicrobial efficacy

The disc diffusion method was used to determine the inhibition zones of the nanofibrous films against \textit{Staphylococcus aureus} and \textit{Escherichia coli} (Shen et al., 2021b). The 100 \( \mu \)L diluent microbial suspensions (about \( 10^6 \) CFU mL\(^{-1} \)) were gently pipetted and dispersed evenly on the LB medium. The nanofibrous films cut to the diameter of 10 mm discs were placed in the center of the medium. The LB medium was placed in an incubator at 37 °C for 12 h. Three equidistant points from the center of the inhibition zones were measured to obtain average diameters.

2.14. Statistical analysis

Data presented as mean ± standard deviation were obtained from independent experiments conducted in triplicate, and Duncan’s multiple comparison test of one-way
ANOVA was performed using SPSS (version 19.0, IBM Corporation, Armonk, USA). $P < 0.05$ was statistically significant.

3. Results and discussion

3.1 Morphologies of nanofibrous films

Fig. 1 shows the morphologies of PVP, PCL, PCL/PVP (2:1), PCL/PVP (3:1), and PCL/PVP (4:1) nanofibrous films. All the films exhibited uniform and smooth nanofibers, and the average diameters of PVP and PCL nanofibers were 925.6 and 369.1 nm, respectively. The average diameter of nanofibers obtained by mixed spinning of PCL and PVP became smaller than those of the PCL and PVP nanofibers, and decreased with the addition of PCL. This was due to the poor spinnability of PVP, resulting in a large fiber diameter, and the addition of PCL increases the spinnability of the solution, leading to finer fibers (Wang et al., 2022). As the addition of PVP reduced the viscoelasticity of the solution, the PCL/PVP fibers were also smaller in diameter than pure PCL fibers (Wang et al., 2022). Wang et al. (2022) developed MgO/PCL/PVP nanofibers by electrospinning, and also found that the average diameter of PCL/PVP nanofibers was finer than that of pure PCL or PVP nanofibers.
Fig. 1. FE-SEM images and diameter distributions of nanofibrous films: PVP (A), PCL (B), PCL/PVP (2:1) (C), PCL/PVP (3:1) (D), and PCL/PVP (4:1) (E).

3.2 FTIR and XRD spectra analysis

FTIR spectra of the nanofibrous films are presented in Fig. 2A. For the PVP nanofibers, the broad stretching band at 3750 to 3000 cm$^{-1}$ was corresponded to O-H and N-H stretching vibrations; the characteristic peak at 1668 cm$^{-1}$ was related to C=O stretching vibrations; and the characteristic peak at 1495 cm$^{-1}$ was related to the C-N bond stretching vibrations and N-H bond flexural vibrations (Kowalonek and Kaczmarek, 2010). For the PCL nanofibers, characteristic peaks were recorded at 2950 and 2869 cm$^{-1}$, 1735 cm$^{-1}$, 1296 cm$^{-1}$, 1240 cm$^{-1}$, and 3442 cm$^{-1}$, which were corresponded to the C-H stretching vibrations, C=O stretching, C-O and C-C stretching, C-O-C stretching, and the combined stretching vibration of O-H and N-H groups, respectively (Zou et al., 2020). The characteristic peaks of PVP and PCL nanofibers could be observed in the PCL/PVP nanofibers, indicating the success of mixed spinning of PCL and PVP. In addition, no new characteristic peaks were observed in PCL/PVP nanofibers, therefore it could be concluded that there are no new chemical bonds in
FTIR spectra of PCL/PVP nanofibers, suggesting the physical interactions between PCL and PVP (Wang et al., 2022).

Fig. 2B shows the XRD pattern of the PVP, PCL, PCL/PVP (2:1), PCL/PVP (3:1), and PCL/PVP (4:1) nanofibrous films. The narrow peaks at 2θ = 21.3° and 2θ = 23.7° were assigned to the semi-crystalline structure of PCL (Xue et al., 2014), and a broad peak at 2θ = 11.5° was observed in PVP nanofibrous film pattern. With the increase of PCL content, the broad peak decreased, indicating the success of mixed spinning of PCL and PVP.
Fig. 2. (A) FTIR spectra and (B) XRD pattern of PVP, PCL, PCL/PVP (2:1), PCL/PVP (3:1), and PCL/PVP (4:1) nanofibrous films.
3.3 Thermal analysis

The DSC curves of the nanofibrous films are shown in Fig. 3A, and the detailed data are shown in Table 1. There were two characteristic endothermic peaks in the DSC curves of PCL/PVP nanofibers, and the melting temperature were marked as $T_{m_{\text{pvp}}}$ and $T_{m_{\text{pcl}}}$, respectively. The melting enthalpy $\Delta H_{m_{\text{pvp}}}$ and $\Delta H_{m_{\text{pcl}}}$ were calculating by integrating the area of the endothermic peaks. The $T_m$ of PVP nanofibers was higher than that of PCL nanofibers, indicating the enhanced thermal denaturation stability (Zhang et al., 2022).

The TGA curves of the nanofibrous films are presented in Fig. 3B and C, and the detailed data are shown in Table S1. The nanofibrous films exhibited two periods of thermal degradation. The first period was before 100 °C, which was associated with the vaporization of residual solvents and bound water (Contardi et al., 2021). The second period was the fastest weight loss period and was in the range of 350 °C to 450 °C, which was belonging to the degradation of PVP and PCL. The results showed that the $T_{\text{max}}$ and the residual weight at 600 °C of PCL nanofibers were 409.5 °C and 2.47%, respectively, and increased with the increase of PVP content, suggesting the improved thermal stability (Zhang et al., 2022).
Fig. 3. (A) DSC and (B and C) TGA curves of PVP, PCL, PCL/PVP (2:1), PCL/PVP (3:1), and PCL/PVP (4:1) nanofibrous films.
Table 1. Detailed data of the DSC and TGA thermograms for the nanofibrous films.

| Sample                  | DSC parameters | TGA parameters |       |       |       |       |
|-------------------------|----------------|----------------|-------|-------|-------|-------|
|                         | T<sub>m</sub> PVP | ΔH<sub>m</sub> PVP | T<sub>m</sub> PCL | ΔH<sub>m</sub> PCL | T<sub>10wt%</sub> | T<sub>max</sub> | W<sub>red</sub> |
|                         | (°C)           | (J/g)          | (°C) | (J/g) | (°C)<sup>1</sup> | (°C)<sup>2</sup> | (%)<sup>3</sup> |
| PVP                     | 93.05          | 240.58         | /    | /    | 397.67 | 437.17 | 11.56 |
| PCL/PVP (2:1)           | 79.14          | 24.47          | 57.37 | 40.17 | 380.17 | 410.17 | 5.78  |
| PCL/PVP (3:1)           | 82.44          | 11.96          | 58.38 | 49.73 | 377.50 | 408.83 | 6.06  |
| PCL/PVP (4:1)           | /              | /              | 58.56 | 106.08 | 379.67 | 409.50 | 2.47  |
| PCL                     | /              | /              | 58.84 | 69.61 | 382.50 | 410.33 | 0.76  |

<sup>1</sup> T<sub>10wt%</sub> the temperature at 10% mass loss.

<sup>2</sup> T<sub>max</sub> the temperature at maximum weight loss rate.

<sup>3</sup> W<sub>red</sub> the residual weight at 600 °C.

3.4 Mechanical properties

The mechanical behaviors of the nanofibrous films were shown in Fig. 4. The elastic modulus, tensile strength, and elongation at break of PVP nanofibrous film were 0.07 MPa, 0.005 MPa, and 9.54%, respectively, and those of PCL nanofibrous film were 0.32 MPa, 0.21 MPa, and 105.5%, respectively. It could be concluded that the mechanical properties of the PCL film were significantly better than the PVP films. For the mechanical behaviors of PCL/PVP nanofibrous films, the elastic modulus, tensile strength, and elongation at break increased with the increase of PCL content. It was worth noting that the mechanical behaviors of the PCL/PVP (4:1) nanofibrous film were better than the PCL film. It could be seen from the SEM images (Fig. 1), the PCL/PVP (4:1) nanofibers had a smaller diameter.
than that of the PCL fibers, and thus possessed a higher fiber density, which led to stronger fiber-fiber interactions, resulting in better mechanical properties (Conte et al., 2020).
Fig. 4. Mechanical behaviors of the films: (A) stress–strain curves; (B) elastic modulus; (C) tensile strength; (D) elongation at break. Different lowercase letters above the error bar indicate significant differences among different nanofibrous films.
3.5 WCA analysis

The hydrophobicity of the nanofibrous films protects the films from being wetted by moisture in the environment. The WCAs of the nanofibrous films at 0 s and 30 s (the equilibration time) are shown in Fig. 5. The PVP nanofibrous film was hydrophilic as the WCA was 88.98° at 0 s and 0° at 30 s, respectively, and the PCL nanofibrous film was hydrophobic as the WCA was 134.42° at 0 s and 131.90° at 30 s, respectively. With the increase of PCL content, the WCA at the equilibration time of the PCL/PVP nanofibrous film increased from 116.43° to 126.20°, indicating the improved hydrophobicity. Ko et al. (2017) and Kang and Choi (2005) pointed out that hydrophobic surfaces reduced the adhesion of yeast cells and hydrophilic microorganisms. Therefore, the PCL-based nanofibrous films possessed the potential in food packaging.

Fig. 5. Water contact angles of the nanofibrous films.
3.6 WVP analysis

The WVP of the nanofibrous films are shown in Fig. 6. The WVP is an important parameter for packaging materials, which is concerned with the moisture transfer between the environment and the packed food (Cui et al., 2017). Due to the hydrophilicity of PVP, the PVP nanofibrous film was dissolved by moisture in the environment, therefore no data for PVP film was obtained. The PCL film exhibited 12.55 g mm/m² h kPa, however, the PCL/PVP films showed significantly lower WVP. This was because that the dissolution of PVP in the PCL/PVP films destroyed the network structure, resulting in a smaller porosity. It was reported that the WVP was directly proportional to the porosity of nanofibrous films caused by nanofiber diameter (Hosseini et al., 2019).

Fig. 6. The water vapor permeability of the nanofibrous films. Different lowercase letters above the error bar indicate significant differences among different nanofibrous films.
3.7 Encapsulation efficiency and *in vitro* release of CGA

As shown in Table 2, the encapsulation efficiencies of the PCL, PCL/PVP (2:1), PCL/PVP (3:1), and PCL/PVP (4:1) films were 59.98%, 57.93%, 57.65%, and 60.05%, respectively, and there was no significant difference. However, the encapsulation efficiency of the PVP film was significantly reduced to 25.71%.

The results of CGA release from the PCL, PVP, and PCL/PVP nanofibrous films are presented in Fig. 7. The PCL, PCL/PVP (2:1), PCL/PVP (3:1), PCL/PVP (4:1), and PVP films containing CGA showed 55.08%, 77.68%, 64.08%, 52.88%, and 76.64% release of CGA within 6 h, and 77.55%, 97.35%, 95.23%, 95.72%, and 99.28% release of CGA at 72 h, respectively, indicating the long-term continuous release. It was worth noting that the cumulative amount of CGA released from the PCL film was significantly lower than that released from other films. This was because that hydrophilic PVP swelled in the system, contributing to the *in vitro* release of CGA (Lin *et al.*, 2019). It could be seen that the PCL/PVP (4:1) film containing CGA had a more balanced release per unit time throughout the release period, indicating that this film possessed the best sustained release. Table S2 show that the release profiles of the PCL/PVP (2:1), PCL/PVP (3:1), PCL/PVP (4:1), and PVP films containing CGA successfully fit the Korsmeyer-Peppas formula as the coefficient values ($R^2$) was 0.815 to 0.872. Moreover, the kinetic constant $K$ was 43.05 to 71.51, and the release exponent $n$ was 0.063 to 0.175, suggesting that the release of CGA was driven by Fickian diffusion (Wang *et al.*, 2017).
Fig. 7. Cumulative CGA release profiles of the nanofibrous films.
Table 2. Detailed data of the encapsulation efficiency, the Korsmeyer-Peppas formula and the inhibition zones for the nanofibrous films.

| Sample       | Encapsulation efficiency (%) | The Korsmeyer-Peppas formula | The average diameters of inhibition zone (mm) |
|--------------|------------------------------|------------------------------|---------------------------------------------|
|              | R²  | n   | k   | S. aureus     | E. coli      |
| PCL          | 59.98±0.47 | 0.312 | 0.060 | 59.24 | 13.57 ± 0.39 | 10.88 ± 0.18 |
| PCL/PVP (2:1) | 57.93±0.38 | 0.815 | 0.063 | 71.51 | 11.20 ± 0.28 | 10.57 ± 0.18 |
| PCL/PVP (3:1) | 57.65±0.78 | 0.860 | 0.115 | 55.72 | 12.61 ± 0.36 | 10.79 ± 0.16 |
| PCL/PVP (4:1) | 60.05±0.48 | 0.872 | 0.175 | 43.05 | 11.19 ± 0.34 | 11.38 ± 0.24 |
| PVP          | 25.71±0.10 | 0.829 | 0.070 | 70.49 | 0 | 0 |

3.8 Antimicrobial efficacy analysis

Fig. 8 and Table 2 show the *in vitro* antimicrobial activity of the nanofibrous films against *S. aureus* and *E. coli*. The results show that the PVP nanofibrous film containing CGA did not exhibit any inhibition against *S. aureus* and *E. coli*. This was due to the low encapsulation efficiency of the PVP film. On the other hand, the PCL, PCL/PVP (2:1), PCL/PVP (3:1), and PCL/PVP (4:1) films containing CGA exhibited inhibitory diameters of 11.57, 11.20, 12.61, and 11.19 cm against *S. aureus* and 10.88, 10.57, 10.79, and 11.38 cm against *E. coli*, respectively, indicating the good antimicrobial activity.
4. Conclusion

In this study, the PVP, PCL, and PCL/PVP nanofibrous films were rapidly developed by SBS for encapsulation of CGA. The SEM results show that the average diameters of PVP and PCL nanofibers were 925.6 and 369.1 nm, respectively, and the average diameters of PCL/PVP nanofibers decreased with the increase of PCL content. The FTIR and XRD proved that the PCL/PVP nanofibers were successfully fabricated by the physical interactions between PCL and PVP. The DSC and TGA curves revealed that the thermal stability was enhanced with the increase of PVP content. The mechanical properties of the PCL/PVP films were better than those of PCL and PVP films due to the stronger fiber-fiber interactions. The PCL/PVP nanofibrous films obtained hydrophobic surfaces due to the addition of PCL, and possessed better water vapor barrier ability than PCL and PVP nanofibrous films. All the nanofibrous films showed the long-term continuous release of CGA, and the release of CGA from PCL/PVP (2:1), PCL/PVP (3:1), PCL/PVP (4:1), and PVP films was driven by Fickian
diffusion. Due to the low encapsulation efficiency, the PVP nanofibrous film did not exhibit any inhibition against *S. aureus* and *E. coli*, but the PCL and PCL/PVP films showed good antimicrobial activity. In summary, the above results suggested that the PCL and PCL/PVP nanofibrous films incorporated with CGA possessed promising prospects in food packaging.
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Declaration of Interest

None.

Author Contributions

Yang Cao: Data curation, Methodology, Formal analysis, Investigation, Writing – original draft, Writing – review & editing. Chaoyi Shen: Methodology, Formal analysis, Writing – review & editing. Zhichao Yang: Methodology, Formal analysis. Zihan Cai: Investigation, Software. Zian Deng: Methodology, Conceptualization. Di Wu: Conceptualization, Supervision, Funding acquisition, Writing – review & editing.

Ethical Approval

This article does not contain any studies with human participants or animals performed by any of the authors.

Informed Consent

Not applicable.
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