Degradation Performance of Electrospun Polylactic Acid/Cellulose Nanocrystalline Composite Fiber Membrane

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Abstract: In this paper, polylactic acid/cellulose nanocrystalline composite fiber membranes were prepared by electrospinning technique. The morphology, thermal properties and in vitro degradation of fiber membranes were analyzed by SEM, FTIR, TG, DSC and other methods. The results showed that both the physiological saline solution and the phosphate buffer solution can degrade the polylactic acid/cellulose nanocrystalline composite fiber membrane, and the degradation effect of the phosphate buffer solution was better. At the same time, it is found that the addition of cellulose nanocrystals improves the pre-degradation rate of composite fiber membranes.

1. Introduction
Polylactic acid is a kind of polymer material with biodegradable properties [1-2], which is widely used in biomedical fields. Polylactic acid is used in an infinite cycle in nature, and its decomposition products are beneficial to the production of crops [3]. It is a very environmentally friendly material. Polylactic acid has good biocompatibility and is often used as a fixed device [4], tissue engineering scaffold [5], surgical suture [6] and drug capsule [7]. Polylactic acid fiber membranes are used as biomedical materials. Fibrous membranes have small voids, hinder the entry of cells, and cannot exchange substances with the surrounding environment. The proliferation and differentiation of cells are affected, and the healing time of wound tissue is prolonged. To solve this problem, the pore size of the fiber membrane can be expanded through the degradation of polylactic acid. Relevant studies have shown that the three-dimensional configuration, crystallinity, chemical bond composition and external environment of polylactic acid are important factors affecting its degradation[8-10].

Cellulose nanocrystals (CNC) have good biodegradability, biocompatibility, reproducibility and high crystallinity. They are good reinforcing fillers and have great application potential, which has caused widespread concern and exploration.

In this experiment, the regenerated polylactic acid was used as the matrix, and the cellulose nanocrystals were used as the filler. The composite fiber membrane was prepared by electrospinning method. The effect of the addition of cellulose nanocrystals on the degradation performance of the polylactic acid composite membrane was investigated by in vitro degradation.
2. Experimental section

2.1 Materials
Polyactic acid (number average molecular weight 47000, weight average molecular weight 113000, PDI = 2.61), Zhejiang Haizheng Company; cellulose nanocrystal, laboratory-made; N, N-dimethylformamide (DMF) (analytical grade, ≥99.5 %), Beijing Tongguang Fine Chemical Co., Ltd.; dichloromethane (DCM) (analytical grade, ≥99.5%), Sinopharm Chemical Reagent Company; saline, laboratory-made; phosphate buffer solution (PBS), pH=7.4 (37 °C).

2.2 Preparation of spinning solution
Cellulose nanocrystals of different qualities and polylactic acid were added to a certain amount of V(dichloromethane): V(N,N-dimethylformamide) was 3:1, and the cellulose nanocrystals were dissolved by stirring at room temperature to obtain 0%, 1.0%, 2.0% and 9% PLA spinning solution. Spinning was carried out under conditions of a spinning voltage of 18 kv, a spinning distance of 18 cm, and a pushing speed of 0.8 ml/h.

2.3 Fiber membrane degradation experiment
The polylactic acid/cellulose nanocrystalline composite fiber membrane prepared by electrospinning technology was weighed to a certain quality, soaked in physiological saline and PBS buffer solution, immersed in a 37 °C oven for several days, and then sampled and dried for weighing and analysis. Weight loss rate = 100% (W1-W0) / W0.

2.4 Characterization
2.4.1 Scanning electron microscopy (SEM): The surface morphology of the spinning fiber membrane was observed by JEOL JSM-6366LV field emission scanning electron microscope. The surface was sprayed with gold.

2.4.2 Fourier transform infrared spectroscopy (FTIR): Infrared spectroscopy analysis of the materials before and after degradation of biomass polyamide was carried out using the German TÜVOR 27 Fourier infrared spectrometer. The test range was 500 cm⁻¹-4000 cm⁻¹.

2.4.3 Thermogravimetric Analyzer (TG): SII Japan Seiko TG/DTG 6300 Differential Scanning Calorimeter was used. Test conditions were 10 °C/min, 30 °C-700 °C, N₂ atmosphere.

2.4.4 Differential Scanning Calorimetry (DSC): 5-10 mg of fiber membrane was placed in a crucible and tested with N₂ as a protective atmosphere from 30 °C to 350 °C.

3. Results discussion

3.1 SEM

Figure 1. Electron microscopic morphology of polylactic acid/cellulose nanocrystalline composite film before degradation
The SEM test results of the polylactic acid/cellulose nanocrystalline composite film are shown in
figure 1. It can be found from figure 1 that the composite film has good apparent morphology, uniform fiber diameter distribution, and no beading, indicating different contents of cellulose. Nanocrystalline and polylactic acid can be used to prepare fiber membranes by electrospinning. At the same time, it can be found that the pore diameter of the composite fiber membrane is large, but its distribution is not uniform. Polylactic acid is a biocompatible material with good biocompatibility and can be used as a biomedical engineering scaffold material to prevent the pore diameter of the fiber membrane. It hinders cell growth, reproduction and adhesion, and prolongs the healing of wound tissue. It can expand its composite fiber membrane pore size by further degradation and broaden its application in the medical field.

3.2 FTIR

![FTIR spectra](image-url)

(a) 

(b) 

(c) 

(d)
The infrared analysis results of the polylactic acid/cellulose nanocrystalline composite fiber membrane before and after degradation are shown in figure 2. It can be seen from figure 2 that the absorption peak of polylactic acid at 2295 cm\(^{-1}\) corresponds to the C-H stretching vibration of the methyl group, 1440 cm\(^{-1}\). The absorption peak at 1360 cm\(^{-1}\) corresponds to CH\(_3\) bending vibration, and the strong peak at 1760 cm\(^{-1}\) corresponds to the characteristic absorption peak of ester carbonyl. In figure 2 (a) and figure 2 (b), respectively, polylactic acid fiber membranes were degraded at different times in saline and PBS buffer solutions. It can be found from figure 2 (a) and figure 2 (b) that when polylactic acid fiber membranes degrade in saline and PBS buffer solution for 2 weeks, new absorption peaks appear at 3400 cm\(^{-1}\), which may be hydroxyl groups distributed on the surface of materials after the degradation.

Figure 2 (c) and figure 2 (d) are PLA+1.0%CNC composite fiber membranes which were degraded in physiological saline and PBS buffer solution for different time, respectively. Characteristic absorption peaks of polylactic acid can be found in figure 2 (c) and figure 2 (d). At the same time, it can be found that the 1131 cm\(^{-1}\) is a C1-O-C4 structure in the cellulose nanocrystalline structure. It can be seen from figure 2 (d) that when the PLA+1.0%CNC composite membrane is degraded in PBS buffer solution for 4 weeks, the new absorption peak of the composite membrane near 3340 cm\(^{-1}\) may be related to the hydroxyl group on the surface of cellulose nanocrystals. Promotes the probability of a hydroxyl group reacting with other groups.

Figure 2 (e) and figure 2 (f) are infrared analysis test results of PLA, PLA+1.0%CNC, and PLA+2.0%CNC degradation in physiological saline and PBS buffer for 2 weeks, respectively. From figure 2 (f), it can be found that the PLA and PLA+2.0%CNC composite film has a new absorption peak around 3300 cm\(^{-1}\)-3400 cm\(^{-1}\), which may be caused by degradation of the polymer segment in the composite. Polylactic acid in the composite is broken to form a small molecule polymer with a carboxyl group or a hydroxyl group, and may also be a hydroxyl group on the surface of the cellulose nanocrystal.

3.3 TG
The results of thermogravimetric analysis before and after degradation of polylactic acid/cellulose nanocrystalline composite fiber membrane are shown in figure 3 (a) and figure 3 (b) in are polylactic acid degraded in physiological saline and PBS buffer solution for different time. The fiber membrane can be found that the main weight loss temperature of the undegraded fiber membrane is 280 °C -380 °C, and the main weight loss temperature of the degraded fiber membrane is 275 °C -370 °C, and the weight loss temperature range is not obvious.

Figure 3 (c) and figure 3 (d) are PLA+1.0%CNC composite fiber membranes which were degraded in physiological saline and PBS buffer solution for different time, respectively. It can be seen from
figure 3 (c) and figure 3 (d) that the main weight loss temperature of the undegraded composite fiber membrane is between 250 °C and 360 °C, and the main weight loss temperature of the degraded fiber membrane is between 270 °C and 370 °C, which is high in the degradation process. The first degradation of the amorphous zone is related. At the same time, it was found that PLA+1.0%CNC composite fiber membrane degraded in physiological saline and PBS buffer for 4 weeks, and the curve showed weight loss at 0 °C -100 °C, which may be related to the complete non-volatile solvent.

Figure 3 (e) and figure 3 (f) are thermogravimetric analysis test results of PLA, PLA+1.0%CNC, and PLA+2.0%CNC degradation in physiological saline and PBS buffer for 2 weeks, respectively. From figure 3 (e) and figure 3 (f), it can be found that the weight loss temperature intervals of the three weight loss curves are approximately the same, which may be completely related to the undegraded. Comparing the six graphs in figure 3. It can be seen that the final residual amount increases with the prolongation of the degradation time. The degradation experiment causes the amorphous region of the polymer to break and form a small molecule, which is no longer part the original polymer, and the polymer itself changes. Moreover, after the long-term immersion of the degradation liquid and the polylactic acid, a substance having a degradation liquid may remain in the fiber membrane. Therefore, the type of the residue after the degradation of the composite membrane after the thermogravimetric test is different from that of the pure substance, and the residual amount cannot be comparatively analyzed.

3.4 DSC

(a)  
(b)  
(c)  
(d)
The thermal analysis of the polylactic acid/cellulose nanocrystalline composite fiber membrane was carried out before and after degradation, as shown in figure 4. Figure 4 (a) and figure 4 (b) are polylactic acid fiber membranes which are degraded in physiological saline and PBS buffer solution for different time, respectively. From figure 4 (a) and figure 4 (b), it can be found that polylactic acid has a small endothermic peak around 60 °-70 °. This endothermic peak should be the glass transition temperature of polylactic acid. The endothermic peak appearing at around 180 ° is the melting peak of polylactic acid. As can be seen in figure 4 (a), the glass transition temperature and melting temperature of the fiber membrane did not change significantly after the polylactic acid fiber membrane was immersed in physiological saline for 1 week, 2 weeks, and 4 weeks. It can be seen from figure 4 (b) that the glass transition temperature shifts to the left after the degradation of the polylactic acid fiber membrane in PBS buffer for 1 week, 2 weeks, and 4 weeks. The number of endothermic peaks of the fiber membrane did not change. The glass transition temperature did not change significantly, indicating that the polymer segment in polylactic acid did not undergo significant fracture degradation. At the same time, it also showed that the degradation effect of physiological saline solution on polylactic acid was not obvious. The phenomenon that the left shift of the glass transition temperature is lowered indicates that the PBS buffer solution degrades the polylactic acid and degrades the polymer segment into small molecular segments.

Figure 4 (c) and figure 4 (d) are PLA+1.0%CNC composite fiber membranes which were degraded in physiological saline and PBS buffer solution for different time, respectively. The characteristic endothermic peaks of polylactic acid can also be found in figure 4 (c) and figure 4 (d). It can be seen from figure 4 (c) that when the PLA+1.0%CNC composite membrane is degraded in physiological saline for 1 week, the glass transition temperature of the composite membrane shifts to the left; when the degradation is 2 weeks and 4 weeks, the composite membrane The glass transition temperature appears to shift to the right, and the melting point of the composite film before and after degradation remains substantially unchanged. It can be seen from figure 4 (d) that when the PLA+1.0%CNC composite membrane is degraded in PBS buffer solution for 1 week and 2 weeks, the glass transition temperature of the composite membrane shifts to the left; when it degrades for 4 weeks, the composite The glass transition temperature of the film shifts to the right, and the melting point of the composite film before and after degradation remains substantially unchanged. It can also be seen from figure 4 (c) and figure 4 (d) that the composite fiber membrane has a prolonged degradation time after the addition of the cellulose nanocrystals. The glass transition temperature appears to be shifted left (lower) and then shifted right (raised). It is indicated that the polylactic acid polymer segment in the composite fiber membrane is degraded into small molecular segments, and its regular molecular chain structure is destroyed, so that the glass transition temperature is lowered. The degradation of polylactic acid in the composite film reduces the steric hindrance of the original macromolecules between the molecules of the CNC, which leads to agglomeration between the CNC molecules, which eventually lead to an
increase in the glass transition temperature. At the same time, it can be found that the addition of cellulose nanocrystals accelerates the degradation rate of the composite membrane to some extent.

Figure 4 (e) and figure 4 (f) are thermal analysis test results of PLA, PLA+1.0%CNC, and PLA+2.0%CNC degradation in physiological saline and PBS buffer for 2 weeks, respectively. It can be seen from the figure 4 (e) and figure 4 (f) that the addition of cellulose nanocrystals causes the glass transition temperature of the composite film to shift to the left, and the melting point of the composite film before and after degradation remains substantially unchanged. It was also found that after the PLA+1.0%CNC composite fiber membrane was degraded in physiological saline for 2 weeks, the melting double peak appeared in the thermal analysis result, probably because the carboxyl group on the surface of the polylactic acid interacted with the hydroxyl group on the surface of the cellulose nanocrystal. The degradation solution can not completely break the polymer segment within 2 weeks, and degrade some of the segments of the polymer chain, so that the crystal size and crystallinity of the composite are different. It is also possible that the cellulose nanocrystals do not degrade in the dissolved solution, they themselves agglomerate together, and the types of crystals in the composite material are different.

3.5 Weight loss before and after degradation

![Graph](image)

Figure 5. Weight loss rate of PLA, PLA+1.0%CNC fiber membrane before and after degradation in physiological saline and PBS buffer

Figure 5 is a mass loss of PLA, PLA + 1.0% CNC fiber membrane before and after degradation in physiological saline and PBS buffer. It can be seen from figure 5 that the degradation rate of PLA+1.0%CNC fiber membrane in the degradation solution is faster than that of the PLA fiber membrane in the degradation solution. It was further proved that the addition of cellulose nanocrystals promoted the degradation rate of the composite fiber membrane in the early stage, which was consistent with the DSC results. From the data of the final weight loss rate, it was also found that when the degradation time was 4 weeks, the weight loss rate of the composite fiber membrane degraded in physiological saline was lower than that in the PBS buffer. It was also proved once again that the PBS buffer had a high degree of degradation of the polylactic acid/cellulose nanocrystalline composite fiber membrane and a good degradation effect.

4. Conclusion
The composite fiber membranes of polylactic acid/cellulose nanocrystals were prepared by
electrospinning technique. After several days of degradation by physiological saline or PBS phosphate buffer, the weight loss temperature range of the composite fiber membrane changes, and the glass transition temperature also decreases with the prolongation of degradation time, which is consistent with the results of infrared and thermogravimetric analysis. At the same time, it was found that the addition of cellulose nanocrystals improved the degradation rate of composite membranes based on polylactic acid in the early stage, and broadened the application of composite membranes in biomedical stents.

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