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论文题目： Design and preparation of environmentally friendly disposable medical masks

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论文摘要：

During the worldwide COVID-19 pandemic, people have discarded enormous amounts of non-degradable masks, which has brought serious environmental pollution to the world. To solve this problem, it is critical to develop environmentally friendly disposable masks. In this research, inspired by spider silk predation, a low-cost, high-performance, and fully biodegradable medical mask was designed and prepared using natural polymers (gelatin and cellulose) as the raw materials. Specifically, cellulose napkin with micro-sized fibers and macropore structure is used as the carrier to guarantee high mask strength and following electrospinning; Gelatin nanofibers film with static electricity is made by electrospinning as a barrier layer to efficiently block virus; Rare earth cerium is utilized as a crosslinking agent, rendering the barrier film high strength; Gelatin elastomer, as a mask strap, is achieved by casting gelation/glycerol solution. I have explored the composite method of cellulose napkin and gelatin nanofiber film to prepare a mask. This mask is low-cost due to the low price of gelatin and napkin and the simple fabrication process. The results showed that the mask filtration efficiency reaches higher than 95% with a respiratory resistance lower than 40 Pa.

Most importantly, this mask can be quickly degraded in moist soil within 1 month. This work would provide a novel approach to solve the global contamination of mask pollution.

关键词：Mask; Gelatin; Biomaterial; Degradation;

目录：

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1. INTRODUCTION

Nowadays, 130 billion disposable masks are discarded every month worldwide under the influence of the COVID-19 pandemic. The traditional disposable medical masks are made of non-degradable polyethylene, polypropylene, or polyester, creating tremendous pressure on the environment, which has become an urgent problem needed to be solved. Therefore, the development of biodegradable masks is of great significance, which could both ensure human health and protect the environment. Thus, it makes me consider what kind of materials could realize both high virus adsorption ability and fast degradation? What kind of structure could realize the balance of the filtration efficiency and breathing resistance? Also, what kind of technique could achieve such a structure?

Enlightened by spider silk predation, I want to construct a porous network with static electricity as a filter layer by the electrospinning method. Furtherly, I choose natural polymers (gelatin and cellulose) as the main materials, which are abundant and natural resourced with low price, and high biodegradability.

Cellulose, composed of glucose, is a macromolecule that is insoluble in both water and common organic solvents. It is the most widely distributed and abundant polysaccharide in nature. A cellulose napkin is used as the support to guarantee high mask strength and the following electrospinning.

Gelatin is a kind of macromolecular protein which is degraded from collagen present in the connective tissue of animals. The raw materials of gelatin mainly include animal bone and skin, which are the by-products of food processing. Owing to its excellent physical and chemical properties, nutritional function and biocompatibility, gelatin could be widely used in food, medicine, cosmetics and many other fields. Under the action of high voltage electric field force, electrospinning technology can continuously produce nanofiber nonwovens, which has been applied to research and develop new filter materials. In particular, the masks produced by electrospinning possess the static electricity conducive to inhibiting the viruses and enhancing the filtration efficiency, ensuring the air permeability of the mask (figure 1).

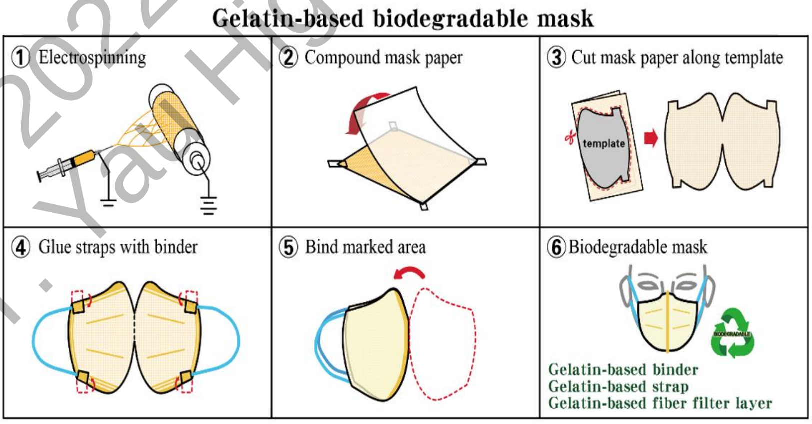

Figure 1. The preparation process of the gelatin-based biodegradable mask.

2. METHODS

2.1 Raw Materials and Reagents

The main material plan used is the acid-process skin gelatin (produced by Fujian Funingpu Gelatin Co., LTD) with a gelation strength of 240 g bloom. Other materials plan to use include: cerium nitrate (produced by Shandong Desheng New Material Co., LTD) and glycerol (produced by Tianjin Damao Chemical Reagent Factory) as additives, DI water as electrospinning solvent; carbitol (produced by Shanghai Jizhi Biochemical Technology Co., LTD.) or trifluoroethanol (produced by shanghai macklin biochemical Co.,Ltd) as electrospinning auxiliary solvent; napkins of different composition, thickness, and the number of layers as a carrier layer.

2.2 Equipment

I used the electrostatic spinning machine (Beijing Yongkang Leye Technology Development Co., LTD), Mask filter performance tester (Chenshi Purification Technology Co., LTD., model SC-FT-1702DYY) and the electronic universal testing machine (Shenzhen Suns Technology Co.,LTD).

2.3 Preparation of gelatin-based electrospinning film

The preparation of gelatin solution: mix a certain amount of gelatin in deionized water, then let the gelatin swell at room temperature for 1 h and dissolve at 60 ℃ water bath.

The gelatin-based electrospinning solution was prepared by adding a certain amount of cerium nitrate and auxiliary solvent (carbitol or trifluoroethanol) into the gelatin solution. The nano-fiber film was obtained after electrospinning for a specific time.

A 10 mL plastic syringe connected to a blunt-ended Luer Lock metal needle loaded the polymer solution (Gauge 22-Sigma Aldrich). Electrospinning conditions were fixed at a flow rate of 0.5 mL/h, an applied voltage of 14 kV, and a distance of 120 mm from the tip to the collector. The operation temperature was 60±5 °C and the humidity was 60%.

2.4 Preparation of the biodegradable mask straps

First, add 0.2 g titanium dioxide nanoparticle and a drop of sky-blue food color into the solution containing 10 g gelatin, 20 g glycerin and 70 g water, and then stir the solution for 30 min by a magnetic stirrer in a water bath at 60 ℃. At last, pour the solution into a semi-cylindrical groove mold with a length of 17 cm and a diameter of 0.5 cm. And the straps were obtained after standing overnight.

2.5 Preparation of the biodegradable mask

The masks were prepared with two layers of napkins as the outer material, one layer of gelatin-based nano-fiber film as the inner material, and the gelatin solution as the binder.

2.6 Performance test methods

The thickness of the filtration layer was measured by a thickness measuring instrument.

The filtration efficiency and respiratory resistance of the napkin, filtration layer, and mask will be measured by the mask filtration performance tester (SC-FT-1702DYY, Chenshi Purification Technology Co., Ltd.). The filtration efficiency (FE) of different masks will be calculated with the following formula:

$$FE = \frac{C_u - C_d}{C_u}$$

C_u and C_d: the mean particle concentrations per bin upstream and downstream, respectively.

Those results will be measured by the tester automatically and the resistance will also be measured at the same time.

To test biodegradability, the mask or the gelatin filtration layer will be put in the soil. The degradation state of the prepared mask will be recorded with photographs.

To test adsorption performance, for the filtration function is contributed by the filtration layer, and the electrostatic adsorption will also enhance the FE. The potential is tested by the potential tester at 25mm away from the filtration layer surface.

3. RESEARCH RESULTS AND DISCUSSIONS

3.1 Study of the spinnability: optimization of gelatin solution

In order to fabricate the gelatin-based filtration layer with the electrospinning method, the spinnability of the gelatin solution was tested and the result is shown in table 1. The 15 wt.% gelatin aqueous solution shows limited spinnability with discontinuous electrospun fibers. By introducing $Ce(NO_3)_3$ additive in the solution, the spinnability was improved and the continuous fibers were obtained. The cross-linking ability of trivalent Ce^{3+} ions could contribute to this good performance. However, the fibers electrospun with gelatin aqueous solution and $Ce(NO_3)_3$ additive show a nonuniform structure with 1 mm diameter beads unevenly distributed on the fibers (Figure 2a) .

Table 1. Spinnability of the gelatin solution with or without $Ce(NO_3)_3$

No.	Additive	Spinnability	Results
1	\	Bad	Discontinuous
2	Ce(NO3)3	Improved	Nonuniform

The high surface tension of the electrospinning solution could contribute to the formation of this beads chain structure. Thus, I further optimized the electrospinning solution by introducing alcohols, including trifluoroethanol and carbitol, as co-solvent which could mix with water in any ratio and reduce the surface tension. Table 2 showed the spinnability results of gelatin solution with co-solvents. The spinnability of the gelatin solution is obviously improved with the help of alcohol co-solvents. Continuous and uniform fibers could be observed in both solutions with trifluoroethanol and carbitol as co-solvents respectively, of which solution with carbitol shows better spinnability and more uniform fibers with a wire diameter of around 100 nm (Figure 2b).

Table 2. Spinnability of the gelatin solution with different solvents

No.	Additive	Spinnability	Results
1	Trifluoroethanol+H2O	Good	Continuous, uniform
2	Carbitol+ H2O	Great	Continuous, uniform

Note: the mass ratio of carbitol to water is 1; the mass ratio of trifluoroethanol to water is 1; the amount of cerium nitrate is 0.86 wt.%.

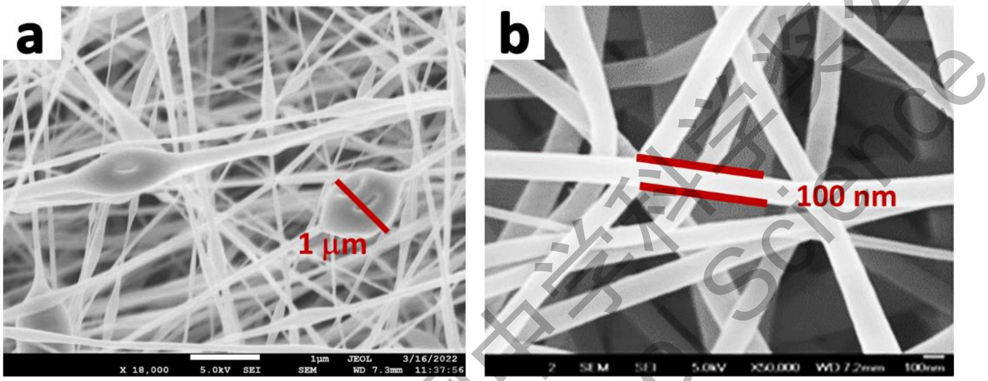

Figure 2. SEM image of gelatin-based filtration layer (a) gelatin aqueous solution with $Ce(NO_3)_3$ additive; (b) gelatin solution with carbitol and water solvent and $Ce(NO_3)_3$ additive

Therefore, an electrospinning solution with carbitol and water as the solvent and $Ce(NO_3)_3$ as an additive were applied for the fabrication of gelatin-based electrospinning film in the following study.

3.2 Effect of gelatin-based electrospinning film's thickness on its properties

Thickness could greatly affect filtration performance of the film. In order to realize a filtration layer with high filtration efficiency and low respiratory resistance, we investigated the effect of gelatin-based electrospinning film's thickness on the filtration performance. By controlling the time of electrospinning, gelatin-based electrospinning films with three different thicknesses were prepared. Each sample were tested 4 times for filtration efficiency and respiratory resistance, and the results were listed in Table 3.

Table 3. Performances of the gelatin-based electrospinning films

No.	Thickness(mm)		Filtration efficiency (%)		Resistance (Pa)	
1	0.064		55.5		12.4	
	0.062	Mean:	56.2	Mean:	12.2	Mean:
	0.067	0.064	55.0	54.7	12.2	12.1
	0.062		51.9		12.2	
2	0.107		95.8		109.2	
	0.121	Mean:	94.7	Mean:	97.0	Mean:
	0.117	0.113	93.6	95.0	94.6	97.2
	0.105		96.0		88.0	
3	0.149		98.9		114.9	
	0.135	Mean:	99.2	Mean:	116.8	Mean:
	0.160	0.152	99.0	99.0	117.3	117.0
	0.162		98.8		118.9	

The gelatin-based electrospinning films (0.064 mm) show a low filtration efficiency of around 54.7% and a low respiratory resistance of around 12 Pa which is far from satisfactory (Table 3). The filtration efficiency of the film gradually increases with the film thickness increasing from 0.064 to 0.152 mm. However, respiratory resistance increases at the same time. With the respiratory resistance higher than 90 pa, breathing will be greatly hindered. Since both filtration efficiency and respiratory resistance increase with the increase of thickness, it is hard to meet both requirements by simply adjusting the thickness. Further optimization is required to decouple these two parameters.

3.3 Study on the gelatin electrospinning film with the napkin as a carrier

To meet the requirement of low respiratory resistance, the thickness of the gelatin electrospinning film should be kept at a relatively low value. I applied a napkin as a carrier which can not only provide mechanical strength but also realize the preliminary filtering of the polluted air. Four common types of napkins were selected and their mechanical strength, filtration efficiency, and respiratory resistance were tested (Table 4).

Table 4. The breaking strength, filtration efficiency, and respiratory resistance of various napkins

Type	Breaking strength（MPa）	Filtration efficiency（%）		Resistance (Pa)	
		1 layer	2 layers	1 layer	2 layers
Cellulose napkin	0.203±0.003	33.4815	34.1119	2.8	4.5
Tissue 1	0.113±0.004	35.6198	41.3285	9.3	22.82
Tissue 2 (Vinda)	0.251±0.015	36.9192	44.4029	12.1	26.7
Tissue 3 (Breeze)	0.147±0.005	34.942	38.5314	11.7	20.4

As shown in table 4, among the four types of napkins, Cellulose napkin and Tissue 2 (Vinda) show higher breaking strength than the other two. And different napkins show similar filtration efficiency with a lower than

3% difference (1 layer) and the effect of the superposition of layers is also not obvious (lower than 10%). A great difference is shown in the respiratory resistance of the napkins. Cellulose napkin provides lower than 3 Pa resistance which is 1/3 of Tissue 1 and 1/4 of Tissue 2 (Vinda) and Tissue 3 (Breeze). Considering these three parameters, cellulose napkins with high breaking strength and low resistance were selected as a carrier layer for the following experiment.

The gelatin-cellulose-napkin composite filtration layer was fabricated by electrospinning the gelatin layer on the cellulose napkin carrier and the thickness was adjusted by controlling the electrospinning time. The morphology of the composite filtration layer was shown in figure 3 and the filtration performance was listed in Table 5. As shown in Table 5, the filtration performances of the filtration layer with the cellulose napkin carrier are much better than that without the cellulose napkin carrier. With thickness at only 0.038 mm, high filtration efficiency of around 97.8% is realized with respiratory resistance lower than 40 Pa which can ensure smooth breathing.

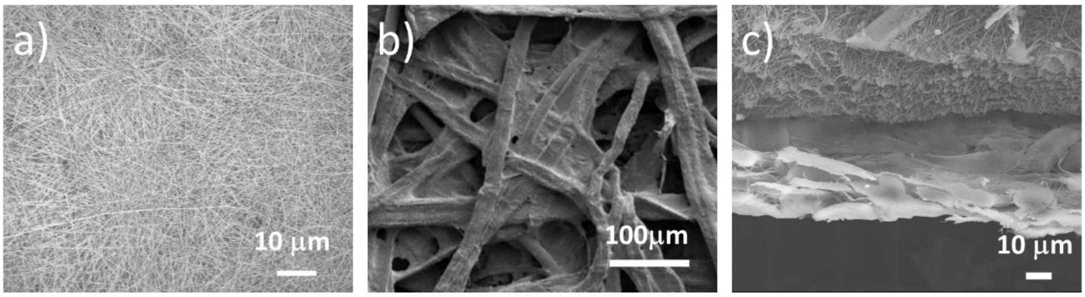

Figure 3. The SEM images of the gelatin-cellulose-napkin composite filtration layer. (a) gelatin side; (b) napkin side; (c) section of the composite filtration layer.

Table 5. Performances of the gelatin-based electrospinning films with the crinkled paper as a carrier

No.	Thickness(mm)		Filtration efficiency (%)		Resistance (Pa)	
1	0.015		82.4		33.8	
	0.019	Mean:	76.9	Mean:	30.1	Mean:
	0.020	0.017	76.9	78.9	31.9	32.0
	0.015		79.5		32.0	
2	0.033		99.1		39.9	
	0.038	Mean:	97.7	Mean:	39.7	Mean:
	0.041	0.038	96.3	97.8	39.9	39.8
	0.041		98.1		39.9	

3.4 Static electricity test

Since the realization of the filtering function of the mask relies on the small pore size and electrostatic adsorption of the filtration layer. Therefore, static voltage is a very important parameter of the filtration film. As shown in Table 6, the electrostatic voltage of the commercial mask is only 0.12 kV, while gelatin-based film without Ce(III) can reach 0.17 kV. The charged functional groups in gelatin molecules could contribute to this good performance. As a biological macromolecular material composed of amino acids, gelatin molecules are rich in carboxyl and amino groups which were positively and negatively charged respectively after being treated by electrospinning technology. By introducing $Ce(NO_3)_3$ additive, the negatively charged carboxyl groups were cross-linked by Ce^{3+} and only the positively charged amino groups were left. Without the internal consumption between positive and negative charges, the electrostatic voltage is largely increased to 0.6 kV which explains the high filtration efficiency of the gelatin-based film with Ce(III). The mechanism was shown in figure 4.

Table 6. The electrostatic voltage of the commercial masks and the gelatin films (GF)

	Commercial mask	**GF without Ce(III)**	**GF with Ce(III)**
Electrostatic voltage	0.12 kV	0.17 kV	0.60 kV

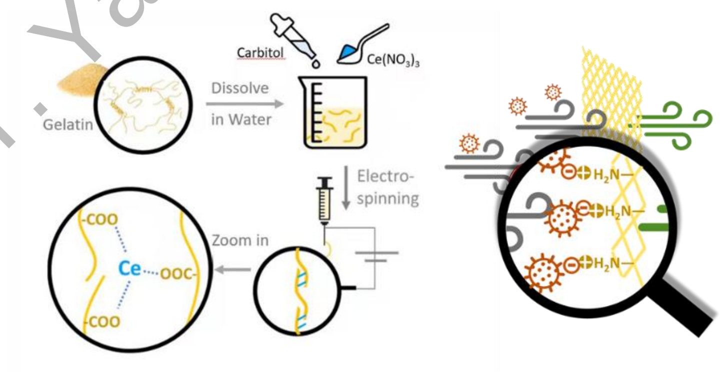

Figure 4. The fabrication process and filtration mechanism of gelatin-based electrospinning films

3.5 Research of the biodegradable properties of the gelatin-based mask

With the high-performance filtration layer, the mask was further fabricated by sticking another cellulose napkin as the inner layer and gelatin elastomer as mask straps with a gelatin binder. Here shows the photos of the gelatin-based mask (Figure 5).

Figure 5. The photo of the gelatin-based mask

Figure 6 shows the degradation process of the gelatin-based nanofiber film and gelatin-based mask. Both gelatin-based nanofiber film and mask can be clearly seen when first buried in the soil. Within 7 days, the nanofiber film rapidly degraded and disappeared. And it takes 4 weeks for the mask to be fully degraded and no residue was observed which indicates that the gelatin-based mask is fully degradable and environmentally friendly.

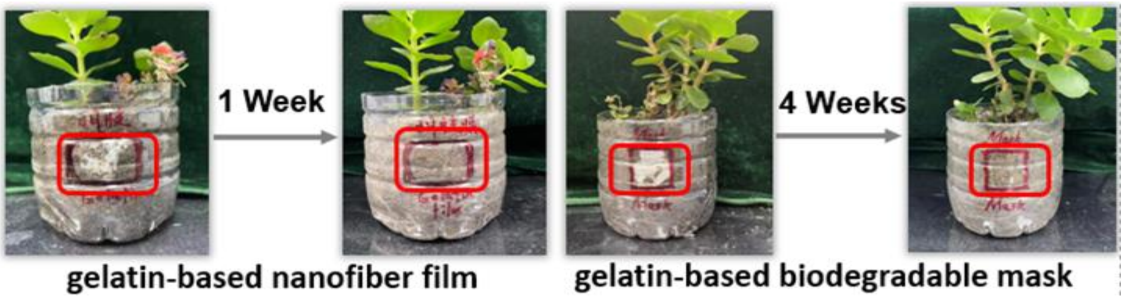

Figure 6. The degradation process of gelatin-based nanofiber film and gelatin-based biodegradable mask

4. CONCLUSION

In this research, a novel biodegradable disposable mask has been successfully prepared using gelatin as raw material and electrospinning with the water and carbitol as solvent (the mass ratio is 1) and the addition of $Ce(NO_3)_3$ (0.86 wt.%). The results show that when the thickness of gelatin-based electrospinning film is 0.038 mm, the filtration efficiency of the mask can be as high as 97.8%. The resistance of the mask is only 39.8 Pa. This research work will provide a new idea for the development of a new degradable mask and a new application for gelatin. This research will contribute significantly to resisting coronavirus pneumonia and improve environmental benefits.

5. REFERENCE

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6. ACKNOWLEDGEMENT

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