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# Functional Polylactic Acid Fiber Membrane with Excellent Fluorescence and Mechanical Properties

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## Abstract

**To impart fluorescent properties to the fiber membrane, polylactic acid (PLA) was used as the matrix, loop-closed Rhodamine B was added for modification, and a PLA/Rhodamine B composite fiber membrane was prepared by electrospinning. The characterization involved an electronic universal tensile tester, Fourier transform infrared spectrometer, ultraviolet-near-infrared spectrophotometer, fluorescence spectrometer, and scanning electron microscope to assess micromorphology, absorbance, fluorescence, and mechanical properties. The results show that the composite fiber membrane with a rhodamine B content of 13.3 wt% has the best comprehensive performance, its diameter is relatively uniform, the average diameter is 20um, and it has the strongest absorption performance of ultraviolet and visible light; the fluorescence intensity after water treatment will change with the rhodamine B The fluorescence intensity of the composite fiber membrane with this content increases with the increase of the content. In the analysis of the mechanical properties of the composite fiber membrane, the composite fiber membrane with this content has the best comprehensive mechanical properties. Therefore, when the rhodamine ratio is 13.3 wt%, the composite fiber membrane not only has good fluorescent properties, but also ensures good mechanical properties of the membrane, providing a simple, low-cost, and environmentally friendly way to prepare fluorescent fiber membranes. It has potential application prospects in the fields of environmental monitoring, biosensing, and smart materials.**

## Keywords

**Composite Fiber Membrane; Closed-loop Processing; Fluorescence; Electrospinning.**

## 1. Introduction

Fluorescent materials represent cutting-edge materials with promising applications; they exhibit color variations in response to external conditions or excitation sources[1-4]. Such materials hold significant potential in various domains, including sensor technology, display technology, nanophotonics, and wearable devices[5, 6]. With the extensive exploration of smart responsive materials, they have garnered widespread attention and thorough investigation in various fields. Gao[7] synthesized a tetrastyrene-functionalized diketone boron complex that initially displayed a bright yellow color but turned red upon grinding. This material exhibited noteworthy aggregation-induced emission (AIE) and mechanochromic behavior. Lee[8] uncovered a hydrochloric conjugated polymer, which incorporates hygroscopic elements into supramolecular assembled polydiacetylene, resulting in a rapidly responsive water-induced color change. This polymer was employed to create

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detailed maps of active sweat pores on fingertips, where even a minimal amount of sweat-triggered water induced a colorimetric reaction, revealing the arrangement of human sweat pores. In recent years, certain materials have been found to exhibit a high sensitivity to water-induced fluorescence effects, making them suitable for water-responsive material applications[9, 10]. Due to the unique properties of these materials, they are often employed in organic solvents and are valuable for detecting trace amounts of water[11-14]. Haihong[15] introduced a new water-responsive color-changing dye, a rhodamine derivative, by modifying rhodamine with functional groups to convert the lactone form into a lactone amide structure. The addition of water, alongside solid acids, can adjust protonation levels, thereby regulating the color and fluorescence of the material, successfully achieving a dual-mode display that switches between color-changing and fluorescence modes. Pyo[8] identified a water-induced fluorescent composite film, which combines water-sensitive fluorescein with a hydrophilic matrix polymer (specifically polyvinylpyrrolidone, PVP). Fluorescein exhibits reversible transformations in both aqueous and dry environments, making it possible to visualize sweat pores by capturing and utilizing the slight moisture from fingertip sweat pores.

In the research of fluorescent materials, expensive reagents, and harsh reaction conditions are mostly required, and there are few fluorescent materials involving fiber membranes. This article develops a simple and novel method to achieve fluorescence of fiber membranes, preparing a Rhodamine B dye that can fluoresce. The modified Rhodamine dye and PLA are electrospinned to obtain a composite fiber material, resulting in a water indicator that can be used for detecting trace amounts of water.

## 2. Experiment

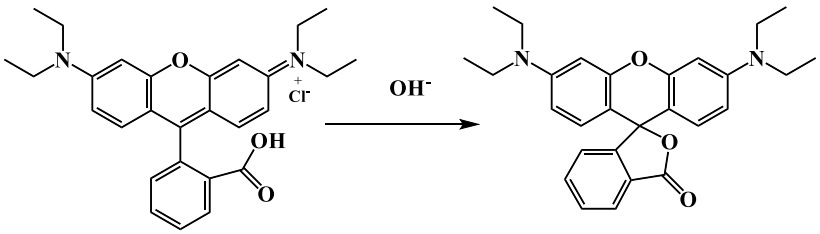
### 2.1 Experimental Materials

The primary experimental materials used in this study were as follows: Rhodamine B hydrochloride (analytically pure, Tianjin Fuyu Fine Chemical Co., Ltd.), N-Hexane (analytically pure, Tianjin Fuyu Fine Chemical Co., Ltd.), Ammonia (25%, Tianjin Fuyu Fine Chemical Co., Ltd.), Methylene chloride (analytically pure, Tianjin Fuyu Fine Chemical Co., Ltd.), N, N-Dimethylformamide (analytically pure, Tianjin Fuyu Fine Chemical Co., Ltd.), Polylactic acid (analytically pure, Dongguan Xiangyi New Materials Co., Ltd.)

### 2.2 Fiber Membrane Preparation

#### 2.2.1 Rhodamine B Closed-Ring Processing

The commercially available Rhodamine B hydrochloride possesses an open-ring structure and requires closure before utilization(figure 1). The procedure involves dispersing Rhodamine B hydrochloride (48g, 0.1mol) in n-hexane (500ml) and adding ammonia solution (25%, 200ml). Stir the mixture overnight, collect the upper purple-red liquid, and conduct rotary evaporation to yield purple-red closed-ring Rhodamine B powder.




**Figuer 1.** Preparation Principle of Closed-Ring Rhodamine B Molecule

#### 2.2.2 Preparation of Composite Fiber Membranes by Electrospinning Method

The preparation of fiber membranes via electrospinning involved using the previously prepared closed-ring Rhodamine B and polylactic acid (PLA) as spinning raw materials. A mixed solvent, consisting of methylene chloride and N, N-dimethylformamide in a volume ratio of 2:1, was used to dissolve the PLA. Closed-loop Rhodamine B and PLA were dissolved in this mixed solvent. The

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PLA content remained constant while varying the closed-loop Rhodamine B content to create spinning solutions with different concentrations of Rhodamine B. The electrospinning conditions were as follows: a voltage of 20kV, an injection speed of 2ml·h-1, a distance to the receiving tin foil of 15cm, and a receiving roller speed of 200r·min-1. Once the electrospinning process was completed, the fiber membrane was carefully peeled off from the tin foil, followed by drying at 40°C for 3 hours. Subsequently, the fiber membranes were stored in a cool and well-ventilated environment. This procedure yielded Rhodamine B-PLA fiber membranes with varying concentrations, specifically at 3.33wt%, 6.67wt%, 10wt%, 13.33wt%, and 16.67wt%.

### 2.3 Testing and Characterization

The microstructure of the composite fiber membrane was observed using a FlexSEM-1000 scanning electron microscope manufactured by Hitachi Corporation of Japan. At 4000-400cm-1, use Thermo Fisher Nicoleti-S50 Fourier transform infrared absorption spectrometer to test commercially available Rhodamine B and closed-loop treated Rhodamine B, obtain the infrared spectrum, observe the characteristic peaks and judge Rhodamine Ming B successfully closed the loop. Take a 10mm×10mm composite fiber membrane and conduct an absorbance test using the Yaou Depeng UV-Visible-Near Infrared Spectrometer DP-3600 to characterize the absorbance of the composite fiber membrane. Use the Zhuoli Hanguang three-dimensional fluorescence spectrometer SmartFluo-Pro to conduct a fluorescence test to characterize the composite fiber membrane. Cut the fiber membrane into slender strips (about 80mm×20mm), and use the Sansi Zongheng Electronic Universal Testing Machine UTM4000 to measure the mechanical properties of the fiber membrane. By analyzing its stress-strain curve, the modulus and modulus of fiber membranes with different Rhodamine B contents are compared.

## 3. Results and Discussion

### 3.1 Morphology and Composition of Composite Fiber Membrane

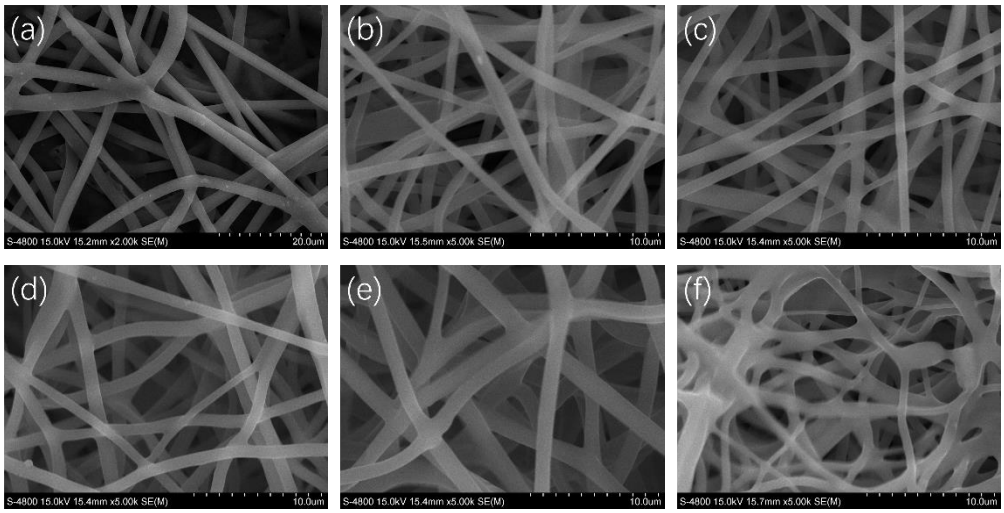


**Figure 2.** Scanning Electron Microscopy Images of Rhodamine B at Various Proportions (a)3.33wt%, (b)6.67wt%, (c)10.00wt%, (d)13.33wt%, (e)16.67wt%, (f)0wt%

The apparent morphology of the electrospun fiber membrane is depicted in the figure. It is evident that the surface of the fiber membrane is uniform, smooth, and devoid of holes, providing comfort, and displaying excellent light absorption characteristics. The microscopic morphology of the fiber membrane, as illustrated in the figure, presents the SEM images of Rhodamine B-PLA fiber membranes with various closed-ring Rhodamine B contents (3.33wt%, 6.67wt%, 10wt%, 13.33wt%, 16.67wt%, 0wt%). From the visual examination and analysis of the fiber diameter distribution, it is evident that all the samples exhibit a fibrous nature, with the fibers intertwining to create a three-

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dimensional network structure. The average fiber diameter for each sample falls within the range of 20 to 30 μm. As the Rhodamine B filler content increases, the fiber diameter gradually enlarges. Specifically, when the Rhodamine B addition is 0wt%, the fiber surface remains smooth, and the fibers maintain excellent continuity. In contrast, as the Rhodamine B content increases to 13.3wt%, the fiber diameter experiences an increase, and the distribution becomes more dispersed.

The chemical composition of the Rhodamine B-PLA fiber membrane was analyzed through infrared spectroscopy (Figure 3). The Fourier-transform infrared absorption spectra of the open-ring Rhodamine B and closed-ring Rhodamine B were obtained using a Fourier-transform infrared spectrometer. The results are presented in the figure. Comparing the absorption peaks of open-ring Rhodamine B and closed-ring Rhodamine B, it is apparent that the closed-ring Rhodamine B exhibits a characteristic absorption peak corresponding to hydroxyl or carboxyl groups in the range of 3400-3500 cm-1. This observation highlights the structural differences between the open-ring and closed-ring forms of Rhodamine B. Specifically, the closure of the ring results in an alkaline base, confirming the successful chemical conversion of Rhodamine B salt from its open-ring to its closed-ring state.

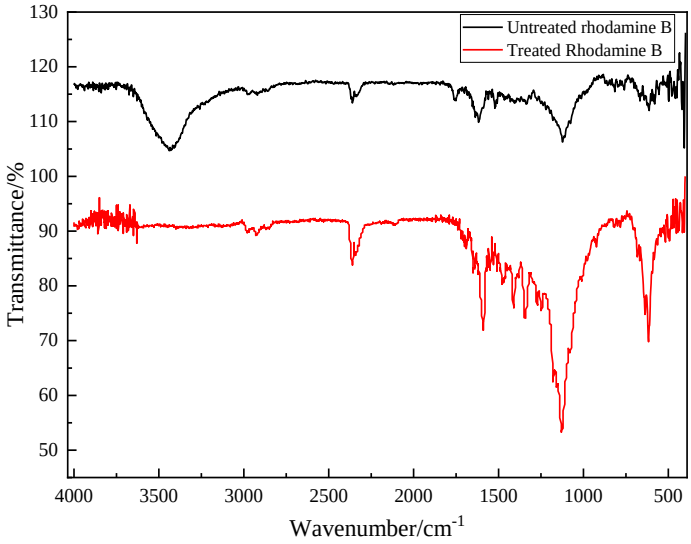


**Figure 3.** Fourier Transform Infrared Spectrum of Open and Closed-Ring Rhodamine B

## 3.2 Effect of Rhodamine B Content on Absorbance

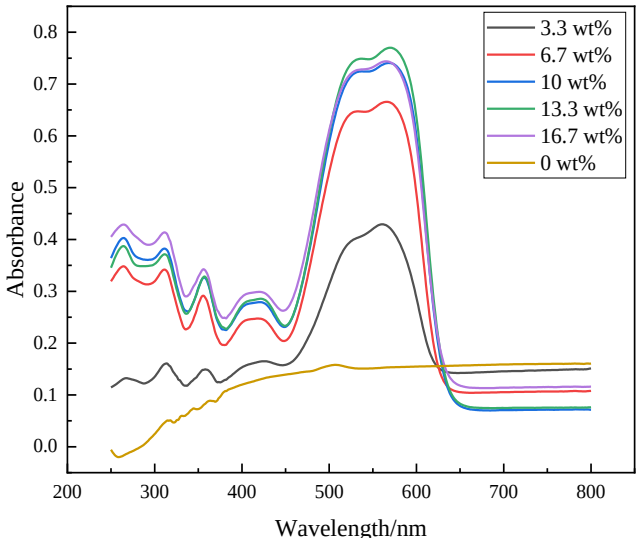


**Figure 4.** UV Absorption Spectra of Rhodamine B Films with Varied Concentrations

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The absorption spectrum of the Rhodamine B/PLA composite fiber membrane was examined using a UV-NIR spectrophotometer (Figure 4). As depicted in the figure, the characteristic absorption peak of the PLA/Rhodamine composite fiber membrane for UV light falls within the range of 500-600 nm. Rhodamine B encompasses a chromophore with a benzene ring and an auxochromophore featuring a phenolic hydroxyl group. When subjected to ultraviolet light irradiation, valence electrons in Rhodamine B make transitions to an excited state. Since electronic energy level transitions invariably involve vibration and shifts between rotational energy levels, the UV-visible absorption pattern exhibits a certain width. With an increase in Rhodamine B content, the absorbance demonstrates a corresponding increase. Notably, when the Rhodamine B content reaches 13.33wt%, the fiber membrane exhibits its highest absorbance at the characteristic absorption peak. This observation suggests that at this particular ratio, Rhodamine B and PLA achieve optimal blending without excessive masking.

### 3.3 Effect of Rhodamine B Content on Fluorescence

Fluorescence treatments of the composite fiber membrane with varying Rhodamine B contents were performed using a fluorescence spectrophotometer (with a test voltage of 700V, a slit width set to 5, and an excitation wavelength of 623nm). The fluorescence excitation spectrum intensity of each sample was measured, and the results are presented in the figure. For the pure PLA fiber membrane without the addition of Rhodamine B, no fluorescence absorption peak was observed. However, upon introducing Rhodamine B, a distinctive fluorescence absorption peak emerged around 558nm, aligning with the theoretical excitation wavelength of pure Rhodamine B within the 500-600nm range. This fluorescence absorption peak proved to be essential for the experiment. It is evident from the figure that the intensity of the fluorescence peak escalates as the Rhodamine B content increases. This phenomenon is attributed to Rhodamine B being the primary luminescent component, thereby establishing a direct relationship between its content and the fluorescence intensity level. Consequently, higher Rhodamine B content corresponds to improved fluorescence performance of the polylactic acid/rhodamine B electrospun fiber membrane.

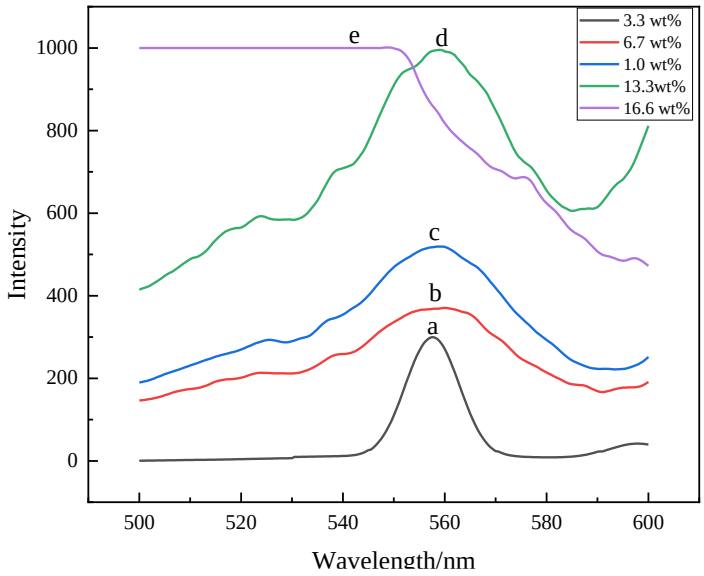


**Figure 5.** Fluorescence Spectra of Rhodamine B Films with Varied Concentrations

### 3.4 Effect of Rhodamine B Content on Tensile Properties

The impact of Rhodamine B on the mechanical properties of the PLA composite fiber membrane was investigated through an electronic universal tensile test. The results reveal that the mechanical properties of the Rhodamine B/PLA composite fiber are slightly lower than those of the pure PLA fiber membrane. Comparing the tensile modulus of composite fiber membranes with varying Rhodamine B contents, as depicted in Figure 6(a), it becomes evident that the modulus is highest

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when the Rhodamine B content reaches 13.33 wt%. At this point, the nanocomposite fiber membrane exhibits its optimal tensile properties. Figure 6(a) also highlights that the introduction of Rhodamine B tends to reduce the tensile strength of the composite fiber membrane. However, the composite fiber membrane with a Rhodamine B content of 13.33wt% demonstrates the highest strength, reaching 2.06 N/(mm)². Thus, it exhibits superior tensile properties. The elongation at the break of the fiber represents its relative elongation at the break. Figure 6(b) shows that adding Rhodamine B tends to decrease the elongation at break. Notably, the composite fiber membrane exhibits robust rigidity but reduced elasticity and toughness when the Rhodamine B content is at 6.67 wt%. In light of the tensile modulus, tensile strength, and elongation at break across various Rhodamine B content levels, it can be inferred that the composite fiber membrane with a Rhodamine B content of 13.33wt% boasts the most comprehensive mechanical properties, providing an optimal balance between flexibility and elasticity.

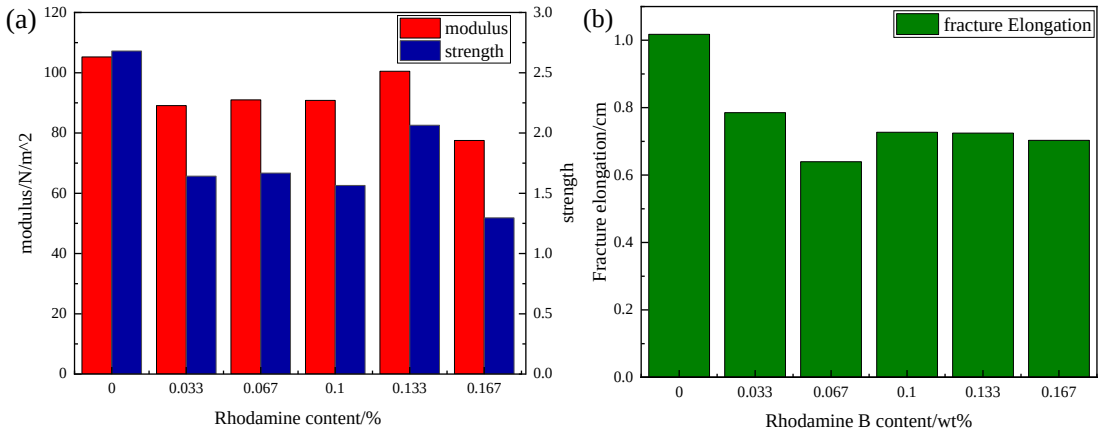


**Figure 6.** Strength/modulus (a), elongation at break (b) of rhodamine B films with different concentrations

## 4. Conclusion

Using the electrospinning method, rhodamine B and polylactic acid were prepared into a composite fiber membrane with fluorescent color-changing properties. The composite fiber membrane was endowed with fluorescent color-changing properties to obtain a good indicator that can detect trace amounts of water in the environment. It is suitable for the indicator fiber membrane.

The surface of the Rhodamine B/PLA composite fiber membrane is uniform and smooth, without holes, and has good continuity; with the addition of Rhodamine B content, the fiber diameter gradually increases, and when the Rhodamine B content is 13.3wt%, the fiber is more uniform, the average diameter of the fiber membrane is 20um; the characteristic absorption peak of the Rhodamine B/PLA composite fiber membrane for ultraviolet light is in the range of 500-600nm. As the content of Rhodamine B increases, the absorbance continues to increase. When the content reaches 13.3wt%, The absorbance reaches the peak, and the content continues to increase, resulting in a masking effect and a decrease in absorbance; the rhodamine B/PLA composite fiber membrane has a texture absorption peak around 558nm, which is consistent with the theoretical excitation wavelength of rhodamine B of 500-600nm. The intensity of the fluorescence peak increases with the tensile property test of the Rhodamine B/PLA composite fiber membrane, showing that the tensile properties of the composite fiber membrane decrease as the Rhodamine B content increases. When the Rhodamine B content is 13.3wt%, the comprehensive tensile performance is the best.

The electrospun Rhodamine B/PLA fiber membrane showcases excellent morphology and fluorescence properties. Different Rhodamine B content levels have varying effects on the fluorescence color-changing properties of the composite film. Notably, when the Rhodamine content is 13.3wt%, the composite fiber membrane excels comprehensively and exhibits high sensitivity to

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trace amounts of water, making it promising for applications in environmental monitoring, biosensing, smart materials, and related fields. This research opens new avenues for exploration and applications in these areas.

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