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Fabrication and Characterization of Photochromic Spirooxazine/Polyvinylidene Fluoride Fiber Membranes via Electrospinning

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Abstract

In this study, photochromic spirooxazine material of *N*-methyl-3,3-dimethyl-9'-hydroxy-spiro [2*H*-indole-2-[3*H*] naphtho [2,1-*b*] [1,4] oxazine] was synthesised. Spirooxazine/PVDF fiber (SPF) membranes with different contents of spirooxazine were successfully prepared by electrospinning. The SPF membranes were characterised by FTIR and SEM. The photochromic properties and contact angle of the SPF membranes were evaluated. The results show that the SPF membranes change from colorless to blue when exposed to UV light, but they revert to their original colour after the UV light disappears. The colour difference and contact angle of the SPF membranes firstly increase and then decrease with a rise in the content of spirooxazine.

Key words: polyvinylidene fluoride (PVDF), spirooxazine, electrospinning, photochromic, hydrophobic.

The encapsulation of spirooxazines within a continuous, polymeric, nanofibrous matrix could confer certain advantages. Spirooxazine-containing nanofibrous membranes have large surface areas, which could increase the sensitivity and reduce the time necessary for spirooxazine to respond to irradiation due to the small diameters.

Nowadays electrospinning has been established as a simple and usable method for drawing polymer fibers with diameters at a nanometer or submicron scale [12-14]. Polyvinylidene fluoride (PVDF) is a commercially available hydrophobic fluoropolymer with low surface energy as well as easy-electronspun and mechanical properties [15, 16]. The choice of PVDF as the electrospun matrix is based on its abundance of hydrophobic fluorine side chains. Due to low surface tension, the vast majority of fluorine-rich groups are expected to migrate onto the fiber surface, which could protect the spirooxazine from adverse environmental effects within (or near) the core of the fibers.

Spirooxazine/PVDF fiber (SPF) membranes can improve hydrophobic properties and increase the specific surface area to improve the reversible sensitivity of colour change and reduce the response time to UV light of spirooxazine due to the small diameters of nanometer scale, as opposed to the micrometer scale in commercial fibers [17]. The SPF membrane can find wide application in flexible optical areas such as optical sensors, optical data storage devices and processing media [18, 19]. To the best of our

knowledge, few reports have focused on the design of SPF membranes by electrospinning.

In this study, *N*-methyl-3,3-dimethyl-9'-hydroxy-spiro [2*H*-indole-2-[3*H*] naphtho [2,1-*b*] [1,4] oxazine] was synthesised. Spirooxazine was characterised by means of FTIR and UV spectrophotometers, and SPF membranes with different contents of spirooxazine were prepared by the electrospinning technique, followed by FTIR and SEM characterisations. The photochromic properties and fading time of the SPF membranes were investigated. The contact angle of the SPF membranes was also evaluated.

Experimental

PVDF (FR-509) was purchased from Xiya Reagent Co., Ltd., China. 2,7-dihydroxynaphthalene (97%) and 1, 3, 3-trimethyl-2-methylene indoline (97%) were purchased from Aladdin Reagent Co., Ltd. All chemicals were of analytical reagent grade.

The synthesis processes of spirooxazine are shown in **Figure 1**.

2,7-dihydroxynaphthalene and sodium nitrate were added to an aqueous solution of sodium hydroxide at -5 °C in a three-necked flask, which was then cooled using ice. Sodium nitrite and sulfuric acid (50%) were dropwise added to the solution under stirring for 70 min. The mixture was stirred at -3 °C for 60 min. The precipitation was filtered and rinsed with deionized water until neutrality was achieved. After that, the precipitation

Introduction

In recent years, photochromic materials have been widely applied in protective ophthalmic lenses, security printing, optical memory and switching, solar energy storage and electrophoretic displays [1,2] because they can change from colorless to colorful when exposed to UV light but can become colorless again after the UV light is removed [2-5]. Among photochromic materials, spirooxazines have received considerable attention due to their intense photo-coloration [6-8], fatigue resistance and ease of synthesis [9-11].

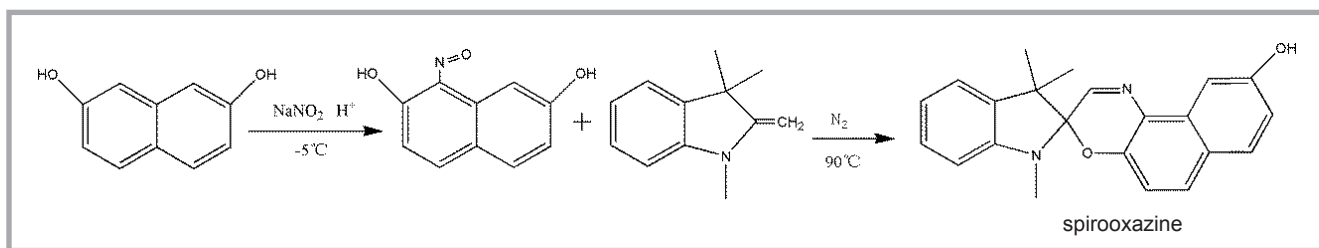


Figure 1. Synthesis processes of spirooxazine.

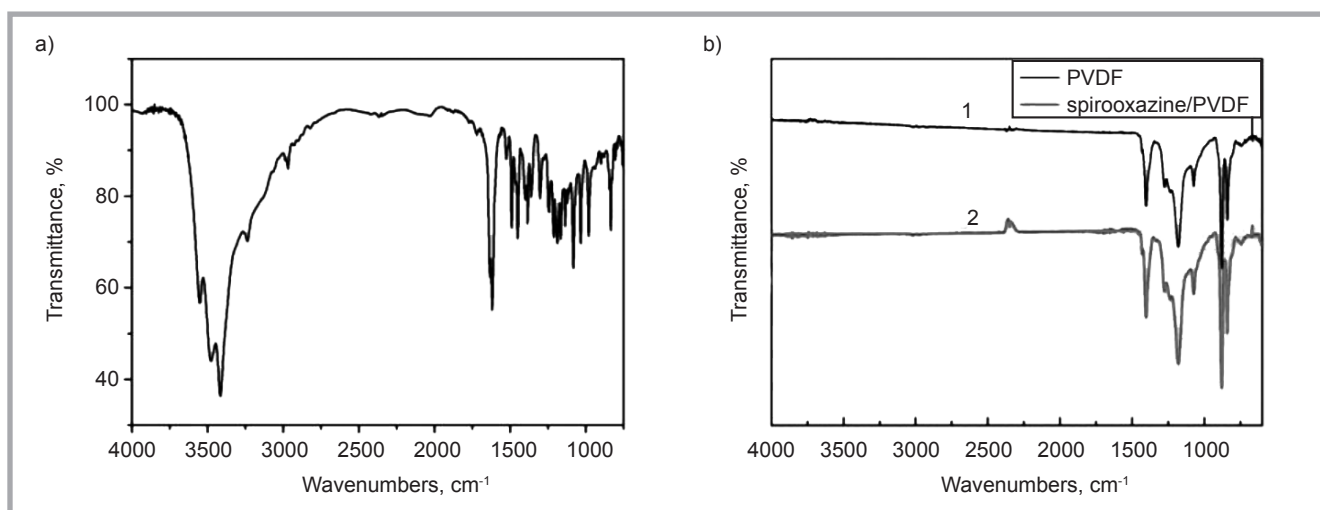


Figure 2. FTIR spectra of a) spirooxazine, (b.1) PVDF and (b.2) SPF membranes.

was dried in a vacuum oven at 50 °C. A red-brown product of 1-nitroso-2,7-dihydroxynaphthalene was subsequently obtained.

1-nitroso 2,7-dihydroxynaphthalene was dissolved in ethanol and the solution heated to 90 °C under a nitrogen atmosphere for 15 min. 1,3,3-trimethyl-2-methylene-indoline in ethanol was dropwise added to the solution during a time period of 30 min, and the mixture was then stirred for 5 h. After that, activated carbon (5%) was added to the mixture, which was then stirred for 15 min. The mixture was filtered and the filtrate evaporated under reduced pressure to remove ethanol. The precipitation was left overnight and rinsed in ethanol. Finally the resultant white products were dried in an oven.

The electrospinning setup consisted of a syringe and needle (ID = 0.5 mm), a ground electrode and high voltage supply. The needle was connected to the high voltage supply, which could generate positive DC voltages up to 10 kV. For the electrospinning of SPF membranes, 1.2 g of PVDF (MW: 2,000,000) and 0.012 g of spirooxazine (1wt%) were firstly mixed together under magnetic stirring and then

dissolved in 8.8 g of N, N-Dimethylformamide (DMF)/acetone (7:3 wt./wt.) at 40 °C. The 12 wt% spirooxazine/PVDF solution was transferred to a needle spinneret by a syringe pump with a mass flow rate of 0.001 ml/s. The steel needle was connected to an electrode of high voltage supply, and a grounded stainless steel roller was placed at 15 cm distance from the needle tip to collect the fiber membranes. The positive voltage applied to the composite solutions was 10 V. The SPF membranes were carefully peeled off from the stainless steel plate after the electrospinning. For comparison, a pristine PVDF fiber-membrane was also electrospun.

FTIR spectra of the spirooxazine, pristine PVDF and SPF membranes were recorded with a Nicolet 6700 FTIR spectrophotometer, USA. The morphology of the SPF membranes were observed by SEM (JSM-5900LV, Japan). The ultraviolet absorption spectrum of the spirooxazine dissolved in ethanol was obtained by means of a UV spectrophotometer (WFZ UV-4802, USA) with the wavelength changing from 200 nm to 400 nm.

Colour measurement of the SPF membranes was carried out by means of

a spectrophotometer (COLOR I5) under Pulsed Xenon D65 and processed using software with a small aperture. The lightness (L^*), redness/greenness (a^*), yellowness/blueness (b^*) and colour difference (ΔE represent the colour difference of the SPF membranes before and after UV irradiation) were obtained.

The SPF membranes were irradiated for 1 min under UV light using a Pulsed Xenon bulb with an emission maximum of 254 nm to evaluate the photochromic properties. The SPF membranes were immediately transferred to the spectrophotometer and their colour properties measured before and after UV irradiation. Pictures of the SPF membranes before and after UV irradiation were taken by a camera. In order to evaluate the fading behavior of the SPF membranes, they were irradiated with UV light for 1 min, and ΔE values were measured at intervals after removal from the UV light source. The time was recorded as the fading time when ΔE tended to 0. Images of the UV-irradiated SPF membranes after different fading times were taken by a camera.

The contact angle of the SPF membranes was measured by a contact angle analyser

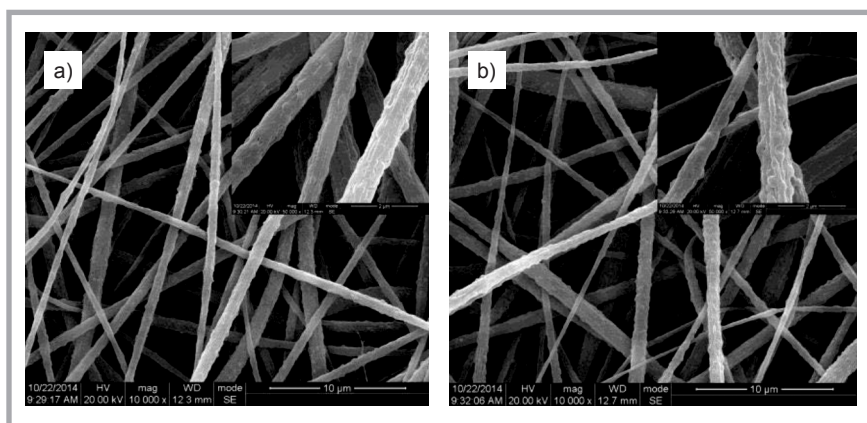


Figure 3. SEM of a) pristine PVDF and b) SPF membranes with different contents of spirooxazine.

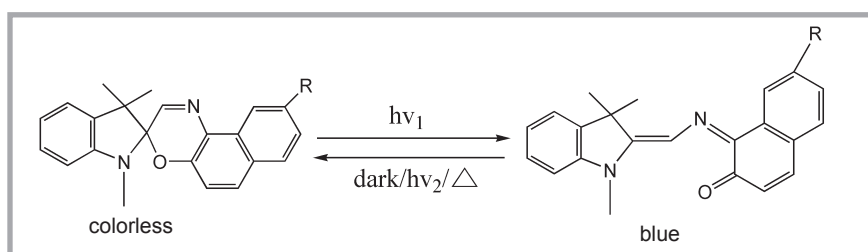


Figure 4. Photocoloration process of spirooxazine.

(HARKE-SPCA×1,China) to determine the hydrophobicity. Five points were chosen for each sample, and the average value was calculated as the result.

Results and discussion

FTIR analysis of the SPF membranes

The FTIR spectrum of spirooxazine is shown in **Figure 2.a**. The peak at 3230.23 cm^{-1} is ascribed to $-\text{OH}$ groups of spirooxazine. The peaks at 1242.66 cm^{-1} and 1080.67 cm^{-1} are attributed to the stretching vibration of functional groups $\text{C}_{\text{spiro}}-\text{O}-\text{C}=\text{N}$. Absorption band 979.63 cm^{-1} is attributed to the stretching vibration of $\text{C}_{\text{spiro}}-\text{O}$ [14]. The stretching vibration of $\text{C}=\text{N}$ is observed at 1632.59 cm^{-1} . Peaks at 1618.00 cm^{-1} and 1527.39 cm^{-1} are assigned to the stretching vibrations of $\text{C}=\text{C}$ in the naphthalene ring. The characteristic absorption peak of $\text{N}=\text{O}$ (aromatic monomer)

is observed at 1531.25 cm^{-1} . Peaks at 1489.39 cm^{-1} and 1449.41 cm^{-1} are assigned to symmetrical and asymmetrical stretching vibration of the naphthalene ring. Peaks at 1300.15 cm^{-1} and 1242.66 cm^{-1} are assigned to the stretching vibration of $\text{C}-\text{O}$. That at 1185 cm^{-1} is assigned to the stretching vibration of $\text{Ar}-\text{O}$. Peaks at 898.21 cm^{-1} , 842.04 cm^{-1} and 744.58 cm^{-1} are ascribed to bending vibrations of the aromatic ring. All these absorption peaks indicate that a spiro group exists in the products. Moreover the results confirm the successful synthesis of spirooxazine.

FTIR spectra of the PVDF and SPF membranes are presented in **Figure 2.b**. The peak at 1402 cm^{-1} is ascribed to a variation in the swing vibration of the CH_2 group. That at 1170 cm^{-1} is attributed to the stretching vibration of the CF_2 group. Peaks at 1180 cm^{-1} and 880 cm^{-1}

are assigned to the skeleton vibration of $\text{C}-\text{C}$. Sharp absorption peaks at 976 cm^{-1} , 840 cm^{-1} , 796 cm^{-1} , 763 cm^{-1} and 614 cm^{-1} are assigned to the crystalline phase vibration of PVDF [15]. However, the content of spirooxazine in the SPF membranes is very low (1 wt%), which is lower than the limit of detection by FTIR (3 wt%); thus the characteristic peaks of spirooxazine were not detected.

Morphologies of SPF membranes

Morphologies of the PVDF and SPF membranes are presented in **Figure 3**. The shape of pristine PVDF fibers and SPFs are both circular. However, the surface of SPFs is rougher than that of pristine PVDF fibers, which can be explained by the fact that the small molecules of spirooxazine in SPF membranes influence the arrangement and crystalline phase of PVDF, and the surfaces of fiber membranes appear uneven with the solvent volatilising during electrospinning. The average diameter of pristine PVDF fibers is 640 nm, whereas that of SPFs is 740 nm, which is bigger than that of pristine PVDF fibers because the polarity of spirooxazine is higher than for PVDF. Random spirooxazine molecules influence the arrangement of PVDF chains to make the mixture stronger polar or weaker polar during electrospinning under different drawing forces; thus different diameters appear.

Photochromism of SPF membranes

In order to evaluate the photochromism of the SPF membranes, colour measurements were also carried out using a colour evaluation instrument with a separate UV source. The colour was evaluated using reflectance measurements converted to colour coordinates and colour difference (L^* , a^* , b^* and ΔE) values between before and after UV irradiation using the CIE Lab color space, the results of which are shown in **Table 1**. SPF membranes convert from white to blue under UV irradiation. The colour of the fiber membranes firstly becomes darker and then lighter with an increase in spirooxazine in the SPF membranes. It can be seen from **Table 1** that the lightness (L^*) for pristine PVDF is high; however, it decreases after spirooxazine has been mixed into the fiber membranes. There is no significant change in lightness for SPF membranes before and after UV irradiation. In addition, the background colour of the SPF membranes is darker than for pristine PVDF. Two factors may

Table 1. Color coordinates and ΔE of SPF membranes with different contents of spirooxazine.

Content of spirooxazine, g/l	L^*	a^*	b^*	ΔE
0	93.50	-0.18	-0.23	
0.8	84.64	-2.05	-4.85	10.17
1.0	81.47	-2.97	-4.84	13.19
1.2	80.28	-4.05	-9.19	16.44
1.4	84.78	-1.49	-6.88	11.05
1.6	84.58	-0.45	-1.39	9.00

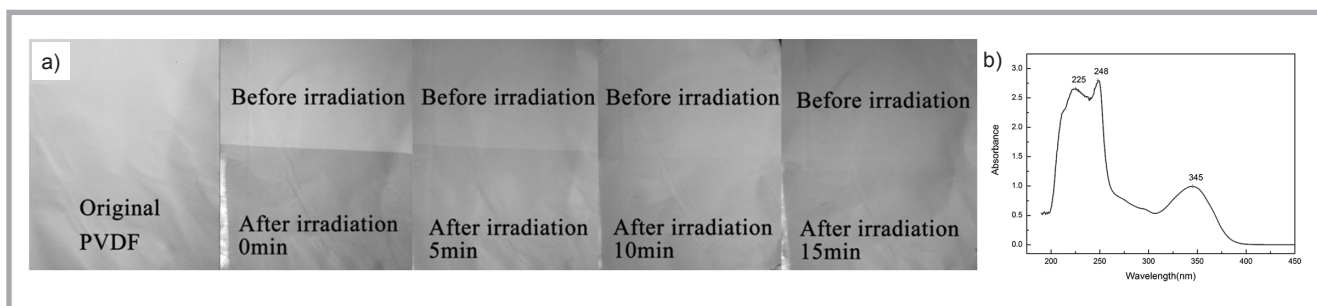


Figure 5. a) Fading time of SPF membranes, and b) UV spectrum of spirooxazine.

influence the background colour on SPF membranes. One is the degree of thermochromism, resulting in the formation of a ring-opened planar coloured form of the spirooxazine, which becomes fixed within the crystalline structure of PVDF, giving rise to a permanent colour. The other factor may be the level of thermal instability of the spirooxazine at elevated temperatures, leading to coloured decomposition products.

The blueness (b^*) of the spirooxazine/PVDF fiber membranes is stronger than that of pristine PVDF after UV irradiation. The spirooxazine/PVDF fiber membranes are moderately pale blue initially but develop a deep blue colour under UV irradiation. The results suggest that spirooxazine/PVDF fiber membranes show excellent photochromism. The phenomena can be explained by the fact that the colourless spirooxazines change to blue cyanines when spirooxazine/PVDF fiber membranes are exposed to UV irradiation, as shown in **Figure 4**. The spirooxazines in molecules of spirooxazine become cyanines of a ring-opened coloured form under UV light, leading to photocolouration of the spirooxazine/PVDF fiber membranes.

After UV irradiation, the photochromic intensity of SPF membranes firstly increases and then decreases with a rise in the content of spirooxazine. However, it can be seen that the colour difference of the SPF-membrane with 1.2 g/l of spirooxazine is the highest of all the fiber membranes after UV irradiation. The results indicate that the SPF-membrane develops the darkest blue under UV irradiation when the concentration of spirooxazine in the electrospinning solution is 1.2 g/l, as shown in **Table 1**, because spirooxazine molecules are too thin to exhibit dark blue at a low content of spirooxazine in SPF membranes. However, SPF membranes also appear shallow blue with a high content of

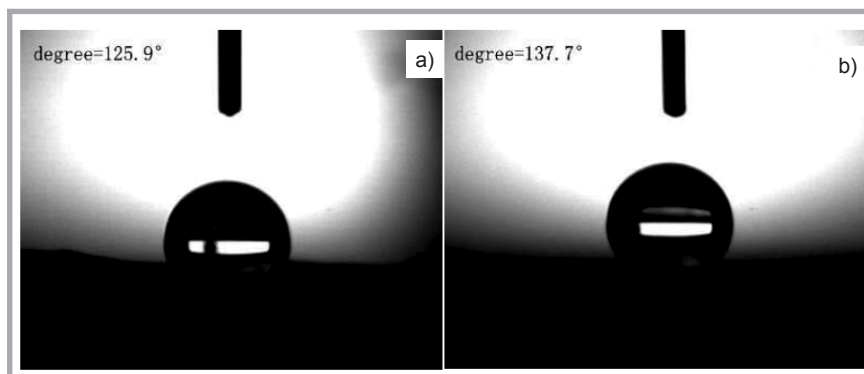


Figure 6. Contact angles of a) PVDF and b) SPF membranes.

spirooxazine. The diffusion of the SPF membrane increases with a rise in the content of spirooxazines. Thus the colour of SPF membranes becomes shallow blue at a high content of spirooxazine.

UV spectrum and fading time of SPF membranes

The fading characteristic of SPF membranes was evaluated by taking digital images every 5 min in the dark at room temperature after the fiber membranes were irradiated for 1 min under UV light. The SPF membranes after fading are shown in **Figure 5.a**. The SPF membrane appears blue after UV irradiation, but this gradually fades in time. The SPF-membrane reverts to being colorless after the UV light is removed after 15 min.

The UV spectrum of spirooxazine dissolved in ethanol is illustrated in **Figure 5.b**. In its ring-closed colorless form, spirooxazine generally has an absorption peak of moderate intensity in the UVA region (320-400 nm), weak absorption in the UVB region (290-320 nm) and very strong UVC absorption (220-290 nm). It can be observed that spirooxazine has two peaks at 248 nm and 345 nm in the UV region due to the absorption of spirooxazine. In addition, spirooxazine shows stronger absorption in the UVC

region, especially at about 248 nm, as compared to that in the UVA and UVB regions, caused by indoline electronic transitions in the molecular structure of spirooxazine. The absorption peak at 345 nm is attributed to naphtho electronic transitions of the molecular structure of spirooxazines. A weak peak at 225 nm is also observed due to the absorption peak of ethanol.

Contact angle of SPF membranes

The surface morphology of the SPF membranes was characterised by contact angle (CA) measurements. The water contact angle on SPF membranes is related to both the roughness of the fiber membranes and chemical components on the fiber surface. However, PVDF is hydrophobic, therefore the water contact angle is determined by the surface roughness. **Figure 6** shows the contact angles of SPF membranes with different contents of spirooxazine. The contact angle of pristine PVDF membranes is 125.9° due to the low values of surface energy of PVDF, and that of the SPF-membrane is 137.7°, indicating that the hydrophobicity of the SPF-membrane is better than that of PVDF membranes. The phenomenon can be explained by the fact that the surface of fibers on spirooxazine/PVDF fiber membranes are rougher than

that of PVDF fiber membranes. Random spirooxazine molecules influence the arrangement of PVDF chains and cause the surface of fibers to be rougher.

Conclusions

In this study, spirooxazine was synthesised from dihydroxynaphthalene, and SPF membranes with different contents of spirooxazine were successfully electrospun. The results show that the SPF membranes possess photochromic properties for 15 min of fading time. In addition, the SPF membranes are hydrophobic at a contact angle of 137.7°. The results indicate that the SPF membranes possess photochromism and hydrophobicity. There is a potential application of SPF membranes in flexible optical sensors, optical data storage devices and processing media.



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