Fabrication a Photoresponsive Film for Controlled Pesticide Release

Qing Xu¹, Guohua Liu¹, Tianhong Feng¹ and Yuanjing Zhou², *

¹ Institute of Biology, Guizhou Academy of Sciences, Guiyang 550009, China
² Institute of Analysis and Testing, Guizhou Academy of Sciences, Guiyang 550002, China
* E-mail: zhuyuanjing-8006@163.com

Abstract. To design and prepare targeted pesticides with environmentally responsive controlled release via compound and chemical modifications has shown great potential in creating novel pesticide formulations. Biological pesticide has spurred demand for efficient and effective delivery systems. In this work, an environmentally photoresponsive controlled release pesticide film was developed by encapsulating biological pesticide with spiropyran-grafted polyacrylic acid polymer as carrier and carboxymethyl chitosan as film-forming agent. Spiropyran-grafted polyacrylic acid polymer carrier had the characteristics of pH and light response. Under the pH response, pesticides were encapsulated. And under the light response, controlled release of pesticides was realized. A series of biological pesticides were encapsulated in the photoresponsive carrier and had high encapsulation rate. The photoresponsive polymer films could therefore be considered an efficient material for application in controlled release systems in agriculture.

1. Introduction

Controlled release formulation of pesticides is highly desirable for improving the performance of pesticides by increasing their efficacy and safety and making them less harmful on ecological environment. Stimulus response controlled release can intelligently respond to the external stimuli and trigger the release of the active ingredients and control pests effectively. [1-6] Photoresponsive pesticide release formulation is environment-friendly and efficient for pesticide delivery applications, which could provide precise control over pesticide delivery. At present, some studies have been done on the photoresponsive controlled release of pesticides. Xu et al. prepared a photocaged pesticide delivery system that could release insecticidal spirotetramat enol form upon light irradiation.[7] Ding et al. synthesized photoresponsive polymeric propesesticide micelles based on photolabile o-nitrobenzyl group for a controlled release of the herbicide dichlorophenoxyacetic acid (2, 4-D).[8] Atta et al. synthesized photoresponsive 2,4-D controlled release agents base on photoresponsive perylene-3-ylmethanol and coumarin to improve the weeding effect.[9, 10] Spiropyrans, as a class of typical photochromic compounds, respond to light and undergo a reversible open-closed transition, that is close for spiropyran (SP) and open for merocyanine (MC). Numerous applications based on their reversible photoresponse and some changes in physical and chemical properties were suggested and examined. [11-13]

In this paper, we prepared an environmentally photoresponsive controlled pesticide release film composed of spiropyran-grafted polyacrylic acid polymer as carrier and carboxymethyl chitosan as film-forming agent. The photoresponsive spirobenzopyran with hydroxyl group was successfully grafted to polyacrylic acid polymer by esterification in the presence of dicyclohexyl carbodiimide
(DCC) and N,N-dimethylaminopyridine (DMAP). A series of biological pesticides were encapsulated in the photosensitive carrier by adjusting the acidity and alkalinity of the solution. The photosensitive controlled release pesticide film was formed by coating method in the glass sheet. This work provides a novel method to fabricate an environmentally photosensitive controlled release pesticide system and might have a huge potential application prospect.

2. Experimental

2.1. Materials and Methods
Carboxymethyl chitosan was prepared by ourselves according to reference 12. 1-(2-Hydroxyethyl)-3,3-Dimethyl-6-Nitrospiro[1(2H)-Benzopyran-2,2-Indoline] (SP), polyacrylic acid, DCC, DMAP, dimethyl sulfoxide (DMSO), validamycin, avermectin, spinetoram, wuyiencin, and all other chemical reagents used in this paper were obtained from commercial sources and were of the highest purity available.

Fourier transform infrared spectroscopy (FTIR) tests were conducted on a Spectrum 100 FTIR spectrometer (PerkinElmer, US) using KBr discs. UV-Vis absorption spectra were recorded using a Lambda 35 UV-Vis spectrophotometer (PerkinElmer, US). High performance liquid chromatography (HPLC) determination was measured by Agilent 1260 high performance liquid chromatography. Deionised water was obtained from a Milli-Q Element water purification system (Millipore Co., Billerica, MA, USA).

2.2. Preparation of Spiropyran Supported Polyacrylic Acid Polymer Carrier
A certain amount of spiropyran and a moderate amount of polyacrylic acid were dissolved in DMSO. After 10 minutes of stirring at room temperature, proper amount of DCC and a little DMAP were added, and then under nitrogen stirred for 48 hours at room temperature. The precipitation was filtered out, and the solvent was evaporated by vacuum distillation. The obtained sample was dissolved in anhydrous methanol, and stayed overnight. The obtained precipitates were filtered, washed with anhydrous methanol, and dried in a vacuum drying oven to get the target product.

2.3. Preparation Pesticide-loaded Photosensitive Controlled Release System
A certain amount of photosensitive carrier was dissolved in deionised water. When the solution was acidic by adding moderate amount of diluted hydrochloric acid, the pesticide was slowly added while stirring. In the dark conditions after stirring for 30 minutes, a certain amount of dilute alkaline was slowly added to make the system neutral. Or the carrier solution was first basic by adding moderate amount of diluted alkaline, and then the pesticide was slowly added while stirring, finally a certain amount of dilute acid was slowly added to make the system neutral.

2.4. Preparation Photo-responsive Controlled Release Pesticide Film
Add appropriate carboxymethyl chitosan and glutaraldehyde to the pesticide-loaded photosensitive controlled release system, and stir at high speed for 30 minutes. The film was formed on glass sheet by casting method, and dried in a vacuum drying oven.

2.5. pH Responsive Property of Photosensitive Carrier
Add appropriate acid or base to the photosensitive carrier solution and make it acidic or alkaline. The pH responsive property was recorded by UV-Vis spectrophotometer.

2.6. Photosensitive Property
The photosensitive property of photosensitive carrier or photosensitive pesticide loaded film was investigated by UV–Vis spectrophotometer. Typically, 10 mL photosensitive carrier solution or photosensitive pesticide loaded film sample was irradiated by the UV light 10 min, and then visible light 15 min. At appropriate time intervals, 2 mL samples of solution were withdrawn from the vials and replaced by 2 mL deionised water. The properties of photo-responsive and photo-controlled
release pesticide of samples were determined by UV–Vis spectrophotometer. The samples without adding photo-responsive carrier were also used as a control.

2.7. Pesticide Loading Properties of the Photoresponsive Controlled Release System
The pesticide loading properties of the photoresponsive controlled release system were determined by UV–Vis spectrophotometer or HPLC. The pesticide encapsulation rate was calculated according to the following equation.

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\text{Pesticide encapsulation rate (\%) = \left(\frac{\text{pesticide loading mass}}{\text{pesticide loading film mass}}\right) \times 100\%}
\]

2.8. Statistical Analysis
In this study, all data are expressed as mean ± SD. Differences between groups were evaluated by one-way ANOVA followed by LSD-test, and P < 0.05 was considered statistically significant.

3. Result and Discussion

3.1. Characterization of Photoresponsive Carrier
Spiropyran with hydroxyl group was successfully grafted to polyacrylic acid polymer by esterification under catalysis of DCC and DMAP. A light pink powder with 80% yield was obtained. The structure of spiropyran-grafted polyacrylic acid polymer was characterized by infrared spectroscopy.

\[
\text{FTIR (KBr, cm}^{-1}\text{): 3290 (-OH), 1732(-C=O), 1615, 1585, 1480 (benzene C-C), 1510 (-NO}_2\text{), 1460 (C-N), 1345 (-NO}_2\text{), 1270, 1125 (C-O-C), 958 (spiro C-O), 840, 805, 755 (-NO}_2\text{).}
\]

3.2. pH Responsive Property of Photoresponsive Carrier

Figure 1 showed the UV-Vis absorption spectra of carrier aqueous solution at different pH values. It could be seen from the figure that the absorption peak intensity of MC structure increases at pH=2 and pH=12, and the absorption peak intensity was higher under alkaline conditions. That is to say, both acid and alkaline conditions could induce SP structure to change into MC structure, and the induction effect under alkaline conditions was greater.

![Figure 1](image)

**Figure 1.** The UV-Vis absorption spectra of carrier aqueous solution at different pH values.

3.3. Photoresponsive Property of Photoresponsive Carrier

Figure 2 gave the peak intensity at 558 nm of maximum absorption wavelength of the carrier irradiated by UV and Vis light at different time. Figure 2a was the variation of maximum absorption peak intensity of carrier aqueous solution irradiated by 365 nm ultraviolet lamp. It could be seen that
the intensity of maximum absorption peak increased with the prolongation of UV irradiation time. The absorption intensity of the maximum peak increased from 0.31 to 0.54 within 9 minutes of UV irradiation. This indicated that the SP structure of photoresponsive carrier was transformed into open MC structure under the stimulation of UV irradiation, and the absorption peak intensity of MC structure increased with the prolongation of ultraviolet irradiation time. Figure 2b showed the change of maximum absorption peak intensity of carrier aqueous solution under Vis light after irradiation by UV for 9 minutes. With the prolongation of irradiation time, more MC structures gradually turned back to close SP structures, so the absorption peak intensity of MC structures gradually decreased. After 9 minutes of ultraviolet irradiation, the absorption intensity of the maximum peak decreased from 0.54 to 0.40 within 9 minutes of Vis irradiation.

3.4. Pesticide Loading Properties of the Photoresponsive Controlled Release Film

![Graph](image)

**Figure 2a.** UV-Vis absorption peak intensity change trend of photoresponsive carrier aqueous solution under UV (365 nm) irradiation.

**Figure 2b.** UV-Vis absorption peak intensity change trend of photoresponsive carrier aqueous solution under Vis irradiation.

![Graph](image)

**Figure 3.** The encapsulation efficiency of the photoresponsive controlled release film on different pesticides.
The encapsulation efficiency of the photoresponsive controlled release film on different pesticides was shown in Figure 3. The encapsulation efficiency of photoresponsive controlled release film on the pesticide tested was wuyiencin > spinetoram > validamycin > avermectins. The highest encapsulation efficiency was on wuyiencin with 85.4%, followed by spinetoram with 73.6%, and the worst encapsulation efficiency was on avermectins with 55.5%. It was related to the physicochemical properties of the pesticides themselves and the structural characteristics of the carrier.

4. Conclusion
An environmentally photoresponsive controlled release pesticide film was fabricated by encapsulating biological pesticide with spiropyran-grafted polyacrylic acid polymer as carrier and carboxymethyl chitosan as film-forming agent. Spiropyran-grafted polyacrylic acid polymer carrier had the characteristics of pH and light response. By adjusting the acidity and alkalinity of the solution, a series of biological pesticides were encapsulated in the photoresponsive carrier and had high encapsulation rate, as high as 85%. This work provides a novel method to fabricate an environmentally photoresponsive controlled release system and would have a huge potential application.

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