Preparation and Properties of Photo-responsive Controlled Release Pesticide Film

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***Abstract*—A photo-responsive controlled pesticide release film system was constructed by using PEG supported spiropyran as a carrier and chitosan as a film-forming additive. The biodegradable film was formed by coating method in the glass sheet. Acetamiprid, a new broad-spectrum insecticide with certain acaricidal activity, was encapsulated in the photo-responsive film reaching encapsulation efficiency as much as 65%. The pesticide release at the same speed was detected from the chitosan film without the photo-responsive carrier, whereas multi-pulsatile pesticide release was observed from the photo-responsive controlled pesticide release film. This work would promote the development of controlled-release pesticide systems.**

Keywords—photo-responsive; controlled release pesticide; biodegradable film

I. INTRODUCTION

The conventional pesticide formulations are facing the single biggest challenge for the sustainable development of the modern green agriculture due to the problems of quickly releasing, low efficacy and serious environmental pollution. [1-3] Controlled delivery technology can effectively resolve the problems. It offers the opportunity to develop formulations which can improve the performance of pesticides by increasing their efficacy and safety and making them environmentally less harmful. Photo-responsive drug release systems are environment-friendly and efficient for drug delivery applications, which can initiate release of the encapsulated drug only at controllable rate, at needed time, and at the suitable site, and have been increasingly investigated, especially in medicine, for the treatment of cancer. [4-7] At present, few studies have been done on the photoresponsive controlled release of pesticides. Ding et al. synthesized photoresponsive polymeric propesticide 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 (Figure 1). Numerous applications based on their reversible color and some changes in physical and chemical properties were suggested and examined. [11-13]

In this paper, a photo-responsive controlled pesticide release system composed of spiropyran compound supported by polyethylene glycol (PEG) was investigated. Biodegradable chitosan was used as a film-forming additive to prepare light response controlled release pesticide film. The photochromic spirobenzopyran with carboxylic group was successfully supported by polyethylene glycols in the presence of dicyclohexyl carbodiimide (DCC) and N, N-dimethylaminopyridine (DMAP). The photo-responsive controlled release pesticide film was formed by coating method in the glass sheet and the properties of controlled release of acetamiprid were studied.

II. MATERIALS AND METHODS

A. *Reagents and Methods*

Chitosan obtained from Shanghai Bo’ao Biotechnology Co. (Shanghai, China) with viscosity-average molecular weight of 500 kDa and 85% degree of deacetylation was purified before using. All other chemical reagents used in this experiment were obtained from commercial sources and were of the highest purity available.

Melting point was measured by X-4 Digital display micromelting point instrument. XE-100E atomic force microscopy produced by PSIA Company of Korea was used to measure the surface structure of the films. 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).

B. *Synthesis of PEG Supported Spiropyran Photochromic Carrier*

A certain amount of PEG-6000 and a moderate amount of 1-(2-carboxyethyl)-2, 3, 3-trimethylindolinobenzopyran were dissolved in dichloromethane. After 10 minutes of stirring at room temperature, proper amount of DCC and a little DMAP were added, and then stirred at room temperature for 12 hours. The precipitation was filtered out, and the solvent was evaporated. The obtained sample was dissolved in acetone, and 6 times volume the petroleum ether was added. Once the impurities were precipitated, they were filtered out. Then treat twice in the same way and dry under vacuum to get the target product.

C. *Preparation Photo-responsive Controlled Release Pesticide Film*

The pesticide film-forming agent was prepared by dissolving chitosan in glacial acetic acid aqueous solution, adding appropriate glutaraldehyde, PEG supported spiropyran photochromic compound, and acetamiprid, and stirring at high speed for 30 minutes. The film was formed on glass sheet by casting method.

D. Characterization of the Photo-responsive Controlled Release Pesticide Film

The pesticide loading properties of the film were determined by UV–Vis spectrophotometer. Firstly, the standard curve of acetamiprid in 50% ethanol solution at 247 nm was drawn. Then, the pesticide loading rate and the pesticide loading amount of the photo-responsive film were calculated according to the formulas (1) and (2), respectively.

Pesticide loading rate (%) = (pesticide loading mass / pesticide loading film mass) *100% (1)

Pesticide loading amount (%) = (pesticide loading mass / pesticide unloaded film mass) *100% (2)

E. Photo-responsive Property

The photo-responsive property of photo-responsive carrier or photo-responsive pesticide loaded film was investigated by UV–Vis spectrophotometer. Typically, 10 mL of 50% ethanol aqueous solution of photo-responsive carrier or photo-responsive 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 of 50% ethanol aqueous solution. 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.

F. 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.

III. RESULTS AND DISCUSSION

A. Synthesis and Characterization of Photochromic Carrier

Spiropyran with carboxylic group was successfully supported by polyethylene glycols in the presence of DCC from the derivatives of indolinospiropyran and polyethylene glycols. Hydroxyl of polyethylene glycol and carboxylic group in photochromic spiropyran acted as the active groups. A light purple waxy solid with 75% yield was obtained. Mp. 37~39 °C. Yet the melting point of PEG-6000 and 1-(2-carboxyethyl)-2, 3, 3-trimethylindolinobenzopyran were 52.5~54.5 °C and 165~167 °C, respectively. FTIR (KBr, cm^{-1}): 2890 ($-CH_2-$), 1730 (-C=O), 1654, 1620, 1580, 1515 ($-NO_2$), 1480 (C-N), 1347 (-NO2), 1275, 1128 (C-O-C), 960 (spiro C-O), 845, 810, 750 (-NO2).

B. Preparation and Characterization of Photo-responsive Controlled Release Pesticide Film

The film containing photochromic carrier, pesticide or photochromic carrier and pesticide was formed on glass sheet by casting method, and the surface structure of the films were measured by XE-100E atomic force microscopy (AFM) produced by PSIA company of Korea under non-contact mode. The phase diagram of AFM is based on the difference between the hardness and softness of the material and the friction force, and it can eliminate the influence of the surface roughness, and avoid the false phase caused by the macroscopic irregularity of the surface topography plane diagram, truly reflecting the composition and structure of the material. Figure 2 (a), (b) and (c) were AFM phase diagrams of chitosan film (CS), chitosan film containing photochromic carrier (CS-PS), chitosan film containing photochromic carrier and pesticide (CS-PS-PT), respectively. On the whole, the particle size distribution tended to be uniform with concave-convex shapes, which indicating that there were interactions among various components.

The standard curve of acetamiprid in 50% ethanol solution at 247 nm was established.

$$Y= 0.981925X-0.00372, R^2 = 0.9996$$

Y is the absorbance value and X is the mass concentration of Acetamiprid in mg/mL. The pesticide loading rate and the pesticide loading amount of the photo-responsive film were 65% and 55% calculated according to the formulas (1) and (2), respectively.

C. Photo-responsive Property of PEG Supported Spiropyran Carrier and Pesticide Loaded Film

The photo-responsive property of PEG supported spiropyran carrier or pesticide loaded film was investigated by UV–Vis spectrophotometer. Figure III showed the photo-responsive property of PEG supported spiropyran carrier before and after being irradiated by UV light. The absorption of indolin at 210-250 nm and benzopyran at 310-350 nm were observed. After irradiation by UV light, the C-O bond of spiropyran ring broke open as the Figure I and showed maximum absorption at 545 nm. This result fully reflected the photochromic properties of spiropyran and provided a guarantee for its use as a photoresponsive material.[11, 12]

Figure II (d) was AFM phase diagrams of chitosan films containing photochromic carrier and pesticide irradiated by UV light for 10 min. It presented a large number of gaps, obviously different from Figure I (a), (b) and (c), which providing a channel for the release of pesticides.[7-10]

Figure IV gave the pesticide film releases pesticide under light control conditions. Multi-pulsatile pesticide release could be achieved by the photo-responsive controlled pesticide release film through UV and visible light irradiation, and approximately 45 % of the loaded acetamiprid was released. Howerer, the pesticide release of chitosan flim without the photo-responsive carrier remained at the same speed, and only 20 % of the loaded acetamiprid was released at about 4 h. These results indicated that this constructed pesticide release system could trigger a slow and much release of acetamiprid from the chitosan film.

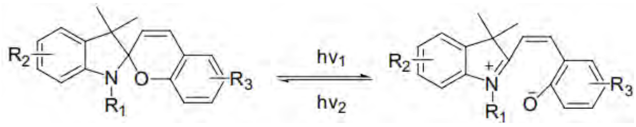
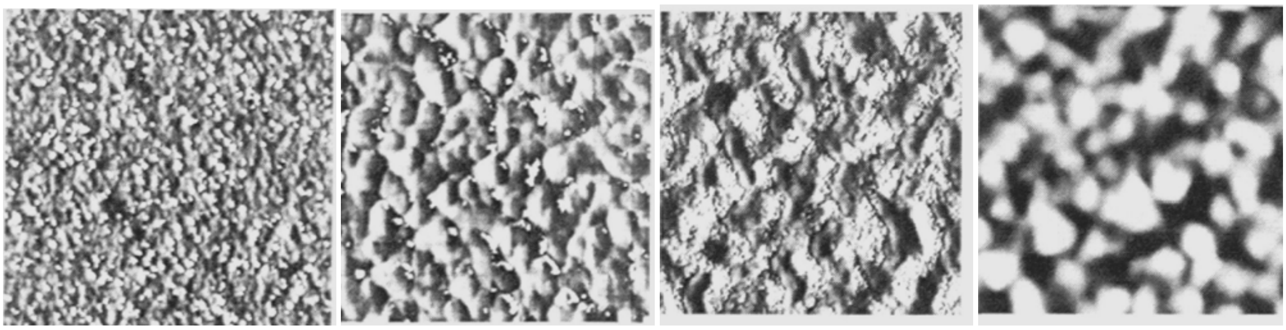


FIGURE I. PHOTO-INDUCED REVERSIBLE OPEN-CLOSED TRANSITION OF SPIROPYRAN



(A) CS (B) CS-PS (C) CS-PS-PT (D) ‘CS-PS-PT’

FIGURE II. AFM PHASE IMAGES OF THE FILMS: (A) CHITOSAN FILM (CS), (B) CHITOSAN FILM CONTAINING PHOTOCHROMIC CARRIER (CS-PS), (C) CHITOSAN FILMS CONTAINING PHOTOCHROMIC CARRIER AND PESTICIDE (CS-PS-PT), (D) CHITOSAN FILM CONTAINING PHOTOCHROMIC CARRIER AND PESTICIDE IRRADIATED BY THE SUN FOR 36 HOUR (‘CS-PS-PT’)

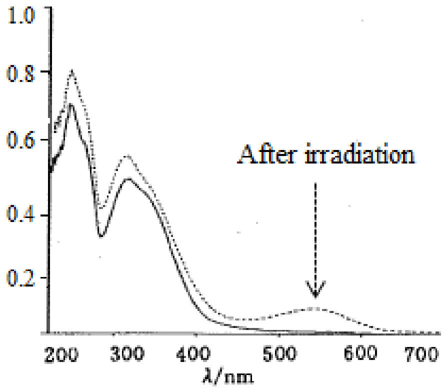


FIGURE III. UV-VIS SPECTRA OF PEG SUPPORTED SPIROPYRAN CARRIER

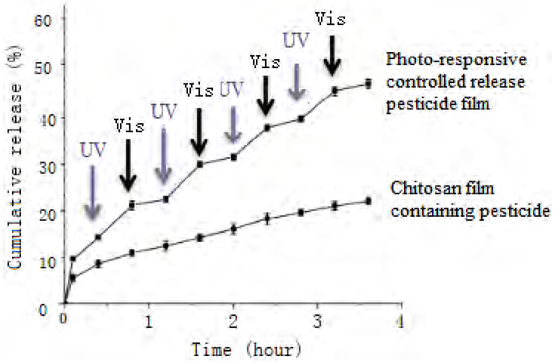


FIGURE IV. CUMULATIVE RELEASE CUVE OF PHOTO-RESPONSIVE CONTROLLED RELEASE PESTICIDE FILM AND CHITOSAN FILM CONTAINING PESTICIDE. PERIODICAL UV AND VISIBLE LIGHT IRRADIATION (UV 10 MIN, VISIBLE 15 MIN) WAS CARRIED OUT

IV. CONCLUSIONS

In this study, a photo-responsive controlled pesticide release film system composed of photo-responsive spiropyran carrier and chitosan was constructed. The photochromic carrier was synthesized by spiropyran with carboxylic group and polyethylene glycols with hydroxyl group in the presence of DCC. The structure of carrier was characterized by FT-IR and melting point. In the glacial acetic acid aqueous solution, the film-forming agent was prepared by adding appropriate glutaraldehyde, and further by casting method the film was formed on glass sheet. AFM photograph investigation showed that the various components of pesticide film system were interactions, which was especially suitable for the encapsulation pesticide.

Research by photo-responsive experiment showed that the PEG supported spiropyran carrier had good photochromic properties. AFM phase diagrams of chitosan films containing photochromic carrier and pesticide irradiated by UV light for 10 min presented a large number of gaps, obviously different from before being irradiated, which providing a good channel for the release of pesticide. The pesticide release from the photo-responsive controlled pesticide release film was approximately 45 % with multi-pulsatile pesticide release mode at about 4 h. And the chitosan film contaning pesticide could release only 20 % the pesticide with the same speed. Thus, a slow release could be achieved from the photo-responsive controlled pesticide release film, suggesting that the photo-responsive controlled pesticide release film may be useful in the delivery of pesticide according to actual needs, and the further investigations are in progress.

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