

Study of polyaniline conducting/electroactive polymer as sensor for some agricultural phosphorus pesticides

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Received: 29 January 2010 / Accepted: 4 August 2010 / Published online: 2 September 2010
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Abstract Due to their wide applications as insecticides, pesticides, chemical warfare agents, etc., detection of organophosphorus compounds is of great importance. This paper deals with application of polyaniline conducting polymer (PANi) as a sensor material for detection of some agricultural organophosphorus compounds that are commonly used as insecticides and pesticides. The compounds employed in this investigation are dichlorvos, trichlorophon, and chlorpyrifos. The effects of some important parameters such as concentration, thickness of the polymer film, etc., on electrical conductivity and conductivity stability for these compounds have also been investigated. In situ electrical conductivity measurements were performed using a standard direct-current (DC) four-point probe technique. It was found that adsorption and desorption of these compounds on PANi film cause measurable change in the resistance of conducting polymers.

Keywords Polyaniline · Organophosphorus · Sensor · Conductivity

Introduction

Electrically conducting polymers are an extremely interesting class of new materials that have attracted considerable

attention in the past decade. Among conducting polymers, polyaniline has been attractive as an intelligent organic polymer for many researchers and scientists due to its ease of preparation, processability, high conductivity, electroactivity, and environmental and thermal stability. Recently there have been some efforts towards its application as a sensor for different kinds of materials, including toxic compounds. Conducting polymers as a class of organic materials can be synthesized by chemical and electrochemical methods using a range of monomers in both aqueous and nonaqueous media. Because of their potential applications, conducting polymers provide a vast field for a number of growing new technologies, such as energy storage devices [1–5], molecular recognition [6–10], ion-exchange membranes [11–13], electromagnetic interference shielding [14–18], optoelectronic devices [19], and as a sensing material for different gases and vapors such as methanol, ethanol, acetone, benzene, NO, NO₂, SO₂, H₂S, and some other toxic gases and vapors [20–25].

Organophosphorus compounds are considered a class of important toxic materials. These compounds have wide applications as insecticides and pesticides in agriculture, and also some of these compounds have applications as chemical warfare agents, mostly as nerve agents, due to their high toxicity. Therefore, detection and sensing of these compounds are of great importance. Previous researchers have used various techniques for detection of these compounds [26–29]. In this work, the sensing properties of polyaniline films for some agricultural organophosphorus insecticides and pesticides such as dichlorvos (DCV, *O,O*-dimethyl 2,2-dichlorovinyl phosphate), trichlorophon (TCF, *O,O*-dimethyl 2,2,2-trichloro-1-hydroxyethyl phosphonate), and chlorpyrifos [CPF, *O*, *O*-diethyl-*O*-(3,5,6-trichloro-2-pyridyl)phosphorothioate]

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have been examined. The four-point probe method was applied to the conductivity measurements.

Results and discussion

Polyaniline has different oxidation states. It is a conducting material in acid-doped partly oxidized state (emeraldine salt form). It is a nonconductive material in both fully reduced and oxidized states, and also in neutral or basic conditions. So, it is expected that any chemicals such as organophosphorus compounds possessing centers with electron deficiency in their structures can affect the oxidation state of the polymer or its electrical properties.

The phosphorus atom in these phosphorus pesticides has little positive charge because of the formation of $p\pi-d\pi$ bonds with $2p$ orbitals of oxygen or sulfur atoms and considering the electronegativity of the contributing atoms. So, it is assumed that compounds with such bonds, which are found in most organophosphorus toxic compounds such as pesticides and also nerve agents and nerve agent stimulants, can affect the electrical properties of PANi films by a p -doping or oxidative mechanism. Also it is expected that this effect on PANi film must be more pronounced in organophosphorus compounds containing P=O bonds than in compounds with P=S bonds, because of the difference in oxygen and sulfur electronegativity. The effect should become stronger (accompanied by an increase in conductivity) on substitution of more electronegative groups on the phosphorus atom and weakened by substitution of groups that can contribute to the π bond with phosphorus and thus reduce the positive charge density on this atom.

In this research it was found that exposure of the polymer film (PANi) to vapors of the examined phosphorus compounds led to an increase in conductivity of the polymer film through the p -doping mechanism. The results obtained from the measurement of conductivity changes versus time of exposure of PANi films of different thicknesses exposed to different concentrations of the vapors of phosphorus test compounds are shown in Figs. 1–10. Our results showed that, in the case of DCV, the conductivity of PANi increased with increasing DCV concentration (Fig. 1). Higher conductivity was also observed when the thickness of the polymer was decreased (Fig. 2).

Increase in conductivity is assumed to be mainly due to the existence of active double bonds bonded to electronegative chlorine atoms and thus creation of another electron-deficient center in this compound. When an initial concentration of DCV of 20 mg/dm^3 was chosen, the conductivity decreased quickly after removing the polymer from exposure to the vapors, and after some initial decrease, the conductivity did not change with time (Fig. 3a). When a lower concentration of DCV was used

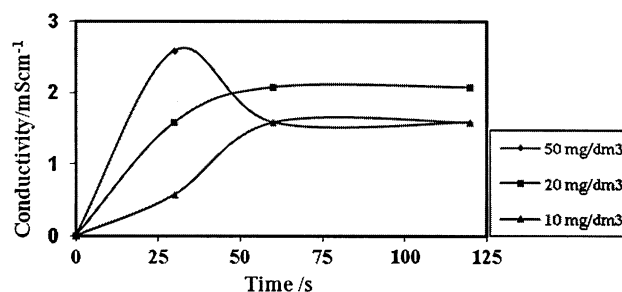


Fig. 1 PANi film conductivity versus exposure time at different concentrations of DCV

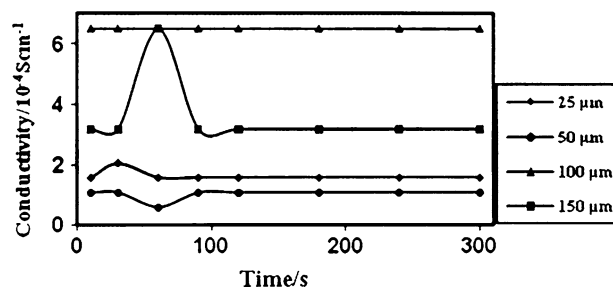


Fig. 2 PANi film conductivity versus exposure time at DCV concentration of 20 mg/dm^3 and exposure time of 30 s

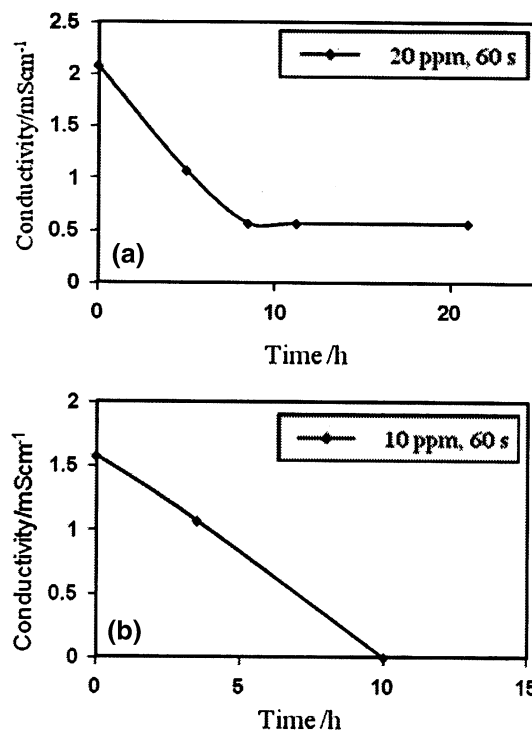


Fig. 3 PANi film conductivity stability with time for DCV at two different concentrations

(10 mg/dm^3), both conductivity and conductivity stability decreased considerably (Fig. 3b).

The effect of exposure time of PANi film to vapors of TCF on conductivity of the polymer is shown in Figs. 4 and 5.

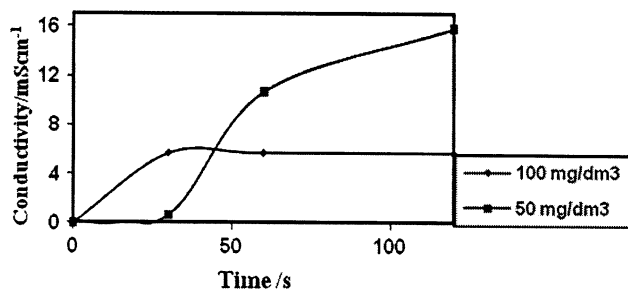


Fig. 4 PANi film conductivity versus exposure time at two different concentrations of TCF

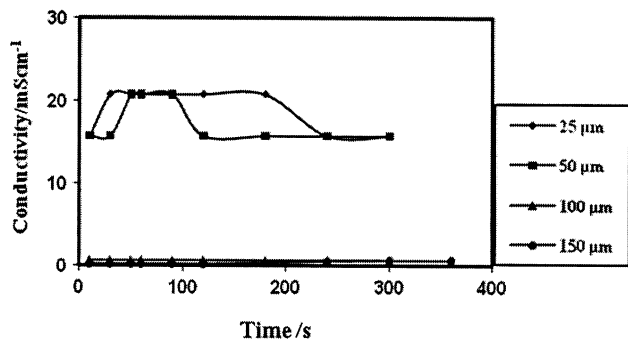


Fig. 5 PANi film conductivity versus exposure time at TCF concentration of 100 mg/dm^3 and exposure time of 60 s

As the results show, lower conductivity was observed compared with DCV under the same conditions. In the case of TCF, conductivity of PANi film decreases as the concentration or the exposure time increases (Fig. 6a–c). Decrease in electrical conductivity can be due to the degradation of the polymer matrix resulting from the high activity of this compound.

In the case of CPF, the obtained results are shown in Figs. 7–10. Lower conductivity and poor conductivity stability were observed with increasing exposure time. The large molecular size of this compound makes its diffusion into the polymer matrix more difficult. The phosphorus atom in this compound is also less electronegative than oxygen, and so it has also less positive charge density compared with the other pesticides investigated in this research.

As our results show (Fig. 7), conductivity of the polymer decreases when the polymer is exposed to CPF vapor, and the required detection time is increased. Some increase in conductivity of the PANi film is observed after its removal from the vapor atmosphere of this compound (Fig. 8). However, it decreases after longer periods because of degradation of the polymer matrix (Fig. 10). This can be attributed to the reactivity and sticky nature of sulfur compounds, as the molecule is first absorbed onto the polymer and in a longer procedure diffuses into the polymer matrix.

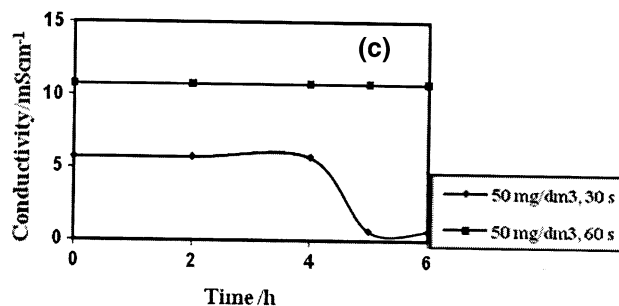
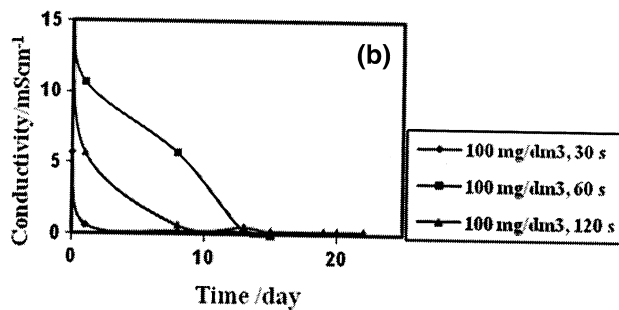
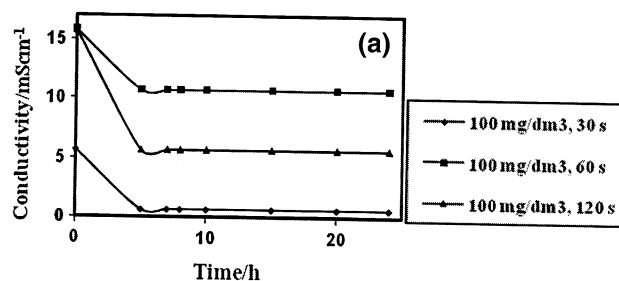


Fig. 6 PANi film conductivity stability with time for TCF for film thickness of a $25 \mu\text{m}$, b $50 \mu\text{m}$, and c $100 \mu\text{m}$

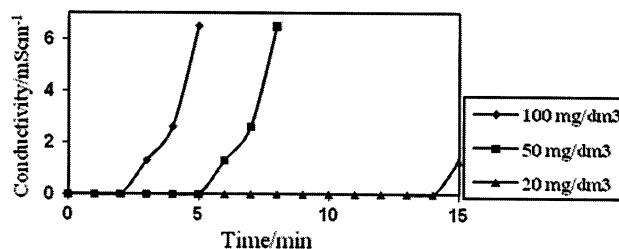


Fig. 7 PANi film conductivity versus exposure time at different concentrations of CPF

Conclusions

PANi film responded to vapors of all tested organophosphorus pesticides. The conductivity of the polymer increased during exposure to the vapors of organophosphorus pesticides. In the case of DCV, the higher increase in conductivity might be assumed to be mainly due to the existence of active double bonds bonded to electronegative chlorine atoms and thus the creation of another electron-deficient center in this compound. The responses of PANi

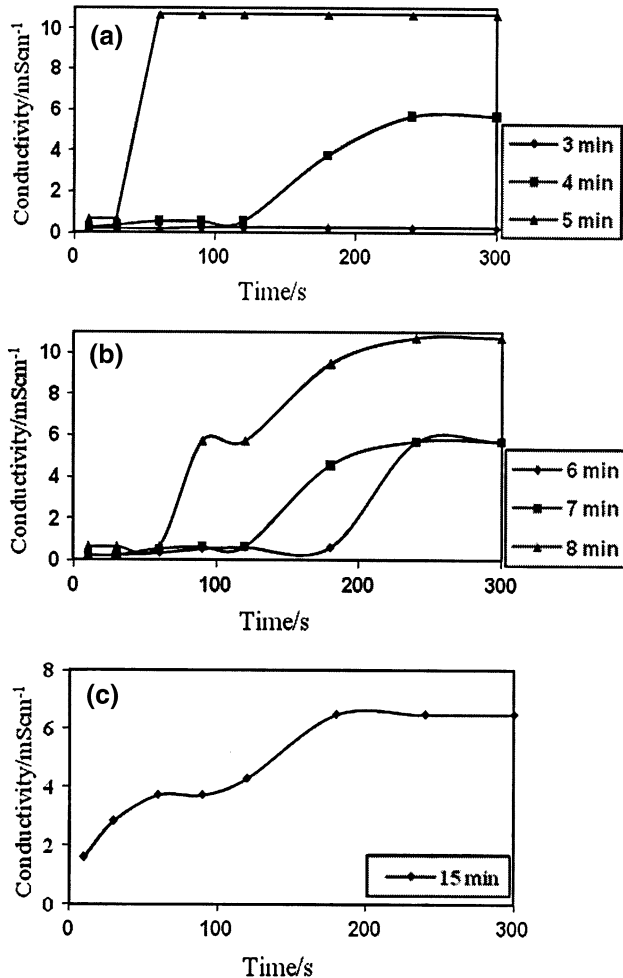


Fig. 8 PANi film conductivity for CPF after different exposure times and at concentrations of **a** 100 mg/dm³, **b** 50 mg/dm³, and **c** 20 mg/dm³

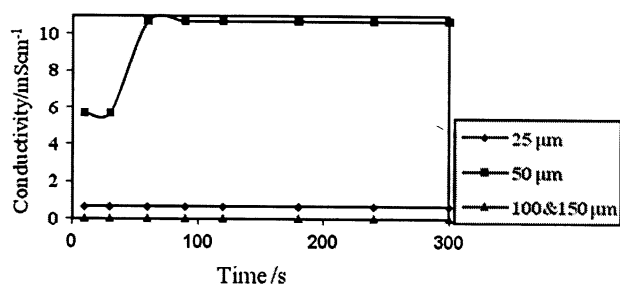


Fig. 9 PANi film conductivity versus exposure time at CPF concentration of 50 mg/dm³ and exposure time of 8 min

films were quite fast and, in case of CPF, the large molecular size and less positive charge on the phosphorus atom led to a need for longer detection or sensing time. Also, PANi films showed good conductivity stability, extending quite long after the exposure. The results show that the best conductivity results can be obtained with film thicknesses of 25–50 μm.

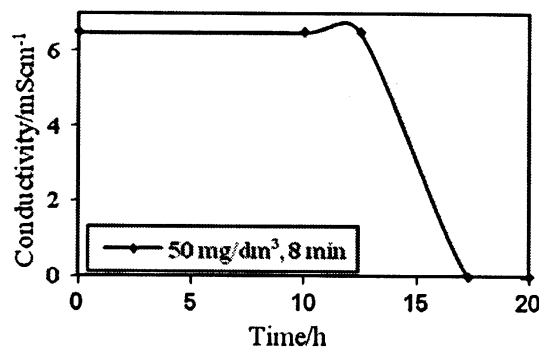
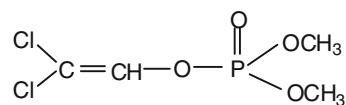


Fig. 10 PANi film conductivity stability with time for CPF for 50 μm

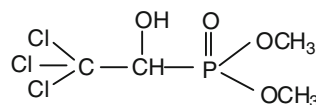
Experimental

Reagents and instrumentation

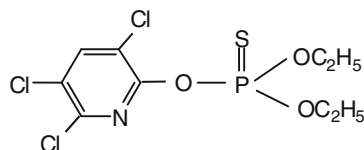
Aniline (Merck) was dried with NaOH and fractionally distilled under reduced pressure from sodium or CaH₂. Phosphorus pesticides (Scheme 1) dichlorvos (DCV, *O,O*-dimethyl 2,2-dichlorovinyl phosphate) and trichlorophon (TCF, *O,O*-dimethyl 2,2,2-trichloro-1-hydroxyethyl phosphonate) were obtained in pure form from samples that had been synthesized in chemical research laboratory in Imam Hossein University from Merck reagents; chlorpyrifos [CPF, *O,O*-diethyl *O*-(3,5,6-trichloro-2-pyridyl) phosphorothioate] was obtained in pure form (standard analytical master) from industrial research center for agricultural pesticides or market. All other materials used in this work were purchased from Merck chemicals and purified, or were prepared by literature methods. Conductivity was measured using a homemade four-point probe device.



Dichlorvos (DCV)



Trichlorophon (TCF)



Chlorpyrifos (CPF)

Scheme 1

Preparation of polyaniline

A protonic acid solution was used for synthesis of polyaniline. For this purpose, two separate 300 cm³ solutions of distilled aniline and ammonium peroxydisulfate (APDS) in 1 M HCl were prepared. The molar ratio of aniline to APDS was 1:1. The vessel containing aniline solution was cooled to -5 °C by an ice-salt bath. The oxidizing agent solution was added dropwise to the monomer while the monomer solution was stirred using a magnetic stirrer. Polymerization was started in a few minutes, and the temperature of the solution increased slightly. The color of the solution gradually became dark, indicating the formation of polyaniline. The solution was stirred at -5 °C for 1 h and then at room temperature for 4 h. Then the solution was put aside for the polymer to settle out. The polymer was filtered out of the solution and washed with distilled water and methanol to remove any possible impurities. The polymer product was dried at 50–60 °C in an oven.

Preparation of emeraldine base

To prepare the polyaniline film, first the undoped form of the polymer, which is called emeraldine base (EB), must be prepared, because this form can be dissolved in the solvent 1-methyl-2-pyrrolidone (NMP). First a solution of 1 M NaOH was prepared, then 10 g PANi powder was added to the stirred solution. The mixture was stirred for 1 h, and then the polymer (EB) was filtered, washed with sufficient distilled water, and dried at 50–60 °C in an air circulating oven.

Preparation of polyaniline film for application as sensor

EB powder (0.50 g) was added to 10 cm³ NMP solvent and stirred for about 1 h to dissolve the polymer. The resulting viscous solution was filtered under vacuum to separate the large particles of the polymer, and a suitable PANi solution was obtained. Films with 40–60 μm thickness were prepared by casting of PANi solution onto a preheated glass slide (5 cm × 10 cm), which was then placed in an oven (70 °C) under reduced pressure (13 mbar). The obtained cast film was washed with a sufficient amount of 10% HCl solution. Then, remaining water was removed by evaporation under vacuum at room temperature.

Sensing experiments

To produce vapor of the sample, a definite amount of organophosphorus sample was put in a cell of definite

volume before putting the PANi film into the cell. The amount of sample was calculated to produce the desired concentration in the cell after conversion to vapor. Then the cell lid and polymer film were put in the cell, and the sample was converted to vapor using mild heating, thus affecting the polymer film in vapor phase. After a definite time, the film was taken out of the cell and its conductivity was measured by a four-point probe device to study the effects of the selected insecticides on the conductivity of the polyaniline film.

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