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The effect of exposure to Pyrinex 480 on the degradation of clear oxodegradable polyethylene agricultural films

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A B S T R A C T

Oxodegradable agricultural films must have predictable lifetimes if benefits associated with their use are to be maximized. This paper presents results examining the change in degradation of oxodegradable films upon exposure to a commonly used insecticide, Pyrinex 480. Pieces of oxodegradable agricultural film, both untreated and treated with different doses of this pesticide in the range of 3.0–10.6 ± 0.5 mg/m^2 of film, were placed in a field environment, gravity ovens at 60, 70 and 80 °C, and an accelerated aging environment that included elevated temperature and exposure to UV light. Degradation of the films was inferred from carbonyl index values calculated using measured infrared absorbance spectra of films collected as a function of exposure time. A delay in oxidation was observed in films treated with Pyrinex 480 relative to untreated films. This delay was most pronounced in environments that included exposure to light. Measurement of the UV absorbance of the pesticide and measurement of its ability to act as a chain-breaking donor or acceptor suggest that Pyrinex 480 achieves its effect on degradation by acting as a UV screener, which has important implications for the use of this type of film where pesticide exposure may be encountered.

1. Introduction

Agricultural films made from polyethylene (PE) have been used to control the microclimate surrounding desirable plants [1] and reduce the need for pesticides and irrigation for more than 50 years [2]. These benefits are offset by the time and cost associated with laying the films at the beginning of the season and collecting and/or disposing of them at the end of the season. The latter of these costs can be avoided without a major change to film manufacturing techniques by using oxodegradable PE films, which break down when exposed to a combination of light, oxygen, and heat at a time determined by the manufacture of the film and the environmental conditions the film experiences.

PE film can be manufactured so that it degrades after a time appropriate for the needs of the crop it is protecting. This is done by limiting the amount of stabilizers, which prevent degradation through stabilization of free radicals, metal chelation, and through absorbance of ultraviolet radiation that may initiate oxidation in PE film [3]. Prodegradants are added to the films during processing to ensure degradation happens within weeks once the stabilizers have been consumed [3]. Control of these additives and associated degradation time of the film is crucial to its success, since a film which degrades too quickly will not provide protection from pests, soil temperature modifications, nor a barrier to evapotranspiration, and a film which degrades too slowly will be an obstacle when harvesting plants at the end of the season.

Exposure of oxodegradable films to some pesticides, either purposefully or by accident, has the potential to disrupt the degradation of the films and make the effective lifetime of the film less predictable. The objective of this work was to determine the effect of treatment with Pyrinex 480, a common insecticide, on the degradation of oxodegradable PE films, as measured in a photo accelerated, thermal accelerated and field environment. To our knowledge, this is the first such study of the interaction of this pesticide with oxodegradable films, in either the lab or the field, but previous research has been conducted on PE films that delineates a gap in knowledge this work may fill [4,5]. A previous study

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examining the effect of pesticides on stabilizers used in PE film manufacture [4] demonstrated that some pesticides may increase the stability of PE films against oxidation while others may decrease it. Another study compared the effect of Chlorpyrifos (the active ingredient in Pyrinex 480) on the UV-induced degradation of clear, stabilizer-free polyethylene film with that of commercial, pigmented agricultural film containing hindered amine stabilizers (HAS) [5]. This study found that even repeated treatment of PE film (without pigment or added stabilizer) with Chlorpyrifos had little to no impact on the oxidation of the film, and insignificant effect on a commercial films' oxidation, elongation at break and average tensile stress at yield [5]. The current study investigates how Pyrinex 480 effects clear films that include prodegradant that allows increased rate of degradation after use.

PE degradation is commonly measured using Fourier Transform Infrared Spectroscopy (FTIR) and inferred from values of the carbonyl index calculated using absorption spectra. The carbonyl index is found by comparing a peak in the absorption spectrum that forms at a wavenumber of approximately 1715 cm^{-1} with the peak at a wavenumber of approximately 1463 cm^{-1}. The peak at 1715 cm^{-1} is associated with C=O stretching vibrations of carboxylic acids/ketones [6,7] which results from oxygen developing in the structure of the PE as degradation proceeds. The peak at a wavenumber of approximately 1463 cm^{-1} is associated with methylene scissoring [8] and acts as a reference which can account for changing film thickness since it remains relatively unchanged during degradation.

The first part of the work described here involves analysis of film degradation in different exposure environments. How Pyrinex 480 may affect film degradation was further examined by testing its ability to act as a stabilizer. Stabilizers are used in the manufacture of PE films to intentionally increase film lifetime by reducing the amount of oxidation that occurs in the film. There are different structural characteristics that are common in stabilizers. These features include multiple OH groups attached to an aromatic ring in an ortho arrangement, a planar structure that allows conjugation, delocalization and resonance effects, and additional functional groups [9]. Chlorpyrifos, the active ingredient in Pyrinex 480, has a pyridine ring that is planar and many functional groups that allow for a variety of different conjugation, delocalization, and resonance effects to occur and therefore may offer stabilizing effects to PE (Fig. 1). Aside from Chlorpyrifos, other ingredients in the insecticide, such as the solvent kerosene, may affect the degradation of these films.

There are three types of stabilizers that are used in the manufacture of oxodegradable PE film pertinent to this study: ultraviolet screeners, which screen UV light and prevent it from being absorbed in the polymer; chain breaking donors, which donate electrons to prevent propagation of free radicals from occurring within the polymer; and chain breaking acceptors, which prevent propagation of free radicals by accepting electrons [10]. Chlorpyrifos may stabilize oxodegradable polyethylene through one or more of these three mechanisms. Previous use of UV absorbance as a means of quantifying the presence of Chlorpyrifos [11] suggests that Chlorpyrifos absorbs UV radiation and may act as a UV screener. Molecules containing chlorine atoms have been shown to inhibit oxidation of carbon [12]. Degradation products of Chlorpyrifos have also been shown to be capable of inhibiting the activity of acetylcholinesterase [13]. Finally, theoretical calculations have demonstrated that in the presence of atmospheric hydroxyl radicals, byproducts of Chlorpyrifos degradation may include O, O-diethyl phosphorothioate and 3,5,6-trichloro-2-pyridinol, which are capable of neutralizing the hydroxyl radical (Scheme 1) [14]. Based on these previous results, there is good reason to expect Pyrinex 480 to stabilize oxodegradable PE film degradation either by acting as a UV screener or by otherwise delaying oxidation.

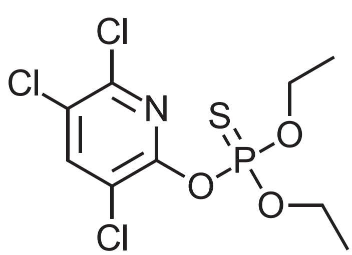
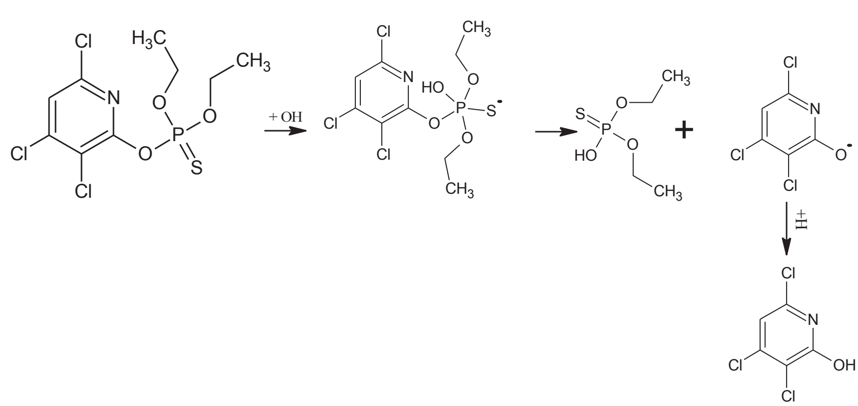


Fig. 1. The chemical structure of Chlorpyrifos, the active ingredient in Pyrinex 480. Features such as the pyridine ring and phosphate functional group may allow the molecule to stabilize free radical reactions.

2. Materials and methods

2.1. Materials

All samples were prepared by cutting pieces from commercially-produced clear PE film which contained 6% by weight of linear low density PE (LLDPE)-based prodegradant master batch, consisting of a blend of transition metal (iron and manganese) carboxylates of fatty acids, typical of film formulated to last between 8 and 12 weeks before disintegration. A potential use for this type of film is to enhance germination of wheat or corn. The short life of the film ensures the film will not be a hindrance when the plants grow. The



Scheme 1. The degradation pathway of Chlorpyrifos when hydroxyl radicals are available. Hydroxyl radicals can be produced during degradation of PE film. As seen in this scheme Chlorpyrifos, the active ingredient in Pyrinex 480, may be able to neutralize the hydroxyl radical and therefore prevent the radical from further propagation in PE.