

The effect of common agrichemicals on the environmental stability of polyethylene films



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ARTICLE INFO

Article history:

Received 1 April 2015

Received in revised form

25 May 2015

Accepted 2 June 2015

Available online 4 June 2015

Keywords:

Polyethylene

Mulch film

Paraquat

Hindered amine stabilizer

Agrichemical

Degradation

ABSTRACT

The impact of commonly used agrichemicals (Paraquat, Mancozeb, Chlorpyrifos and Sulfur) on the environmental stability of polyethylene films has been evaluated under accelerated photo-oxidative conditions. Paraquat and Mancozeb when applied to unstabilized clear polyethylene film, followed by exposure to UV radiation, resulted in direct attack of the polymer, evident by faster rates of oxidation and shorter times to embrittlement compared to a polyethylene control. Reapplication of these chemicals during exposure, as often occurs in agricultural practice, resulted in even faster degradation. In contrast, Sulfur and Chlorpyrifos did not have a significant effect on the photodegradation of exposed unstabilized polyethylene film. When the polyethylene film was pigmented (white top layer containing rutile titanium dioxide and carbon black in the bottom layer) and stabilized with the addition of hindered amine stabilizers (HAS), differences in oxidation susceptibility were seen with repeated exposure to Paraquat showing the most dramatic effect. This was evident by an increased carbonyl index, decrease in elongation at break and an increase in tensile stress at yield compared to a control film and other agrichemical treatments. These studies enable degradation from accelerated consumption of stabilizers by the agrichemicals (and their degradation products) to be differentiated from enhanced photochemical initiation of the polyethylene degradation.

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1. Introduction

Polyethylene mulch films are commonly used in horticulture for a range of crops, including: tomatoes, capsicums and melons [1]. Mulch films must be cheap, easy to process and mechanically tough as they are used as a barrier to suppress weed growth and pest access [2]. The use of mulch films therefore allows lower levels of herbicides and pesticides to be employed. However, agrichemicals are still applied in combination with such films [3], and notably, several sulfur and chlorine-containing agrichemicals have been found to cause accelerated degradation of stabilized polyethylene [4–7]. It has been recognized that this is related to specific chemical reactions with the stabilizers that reduces their effectiveness and shortens service lifetimes.

Polyethylene mulch films are typically exposed to the outdoor

environment for several months up to a year [8] before removal and disposal, and are required to retain their mechanical integrity on collection [1]. If the films have degraded during use in the field, fouling of the machinery used for collection can occur, and the fragments of plastic may disperse at random, providing an environmental hazard. Such wind-blown debris may also pollute rivers and lead to well-chronicled damage to aquatic systems [9]. To obviate this, hand collection may be required at significantly higher cost for the producer.

To prevent degradation caused by exposure to UV and heat, polyethylene mulch and crop propagation films have stabilizers added which either inhibit oxidation (hindered phenols) or retard it (hindered amines) [10]. Both stabilizer types act by interrupting the oxidation of polyolefins. The generally-accepted mechanism of oxidation involves the polymer peroxy radical PO_2^* as the chain carrier. The products from the reaction (1) of the peroxy radical PO_2^* with a reactive hydrogen in the polyolefin (PH) are the polymer hydroperoxide (POOH) and a new alkyl radical (P^*).

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The rapid reaction (2) of the alkyl radical with oxygen regenerates a peroxy radical so the oxidation reaction can continue. This process is still a linear chain reaction, however, and results in the accumulation of POOH as the oxidation product. Such hydroperoxides are stable in the dark at $T < 100^\circ\text{C}$, but can decompose on exposure to UV or high temperatures to initiate further oxidation and ultimately result in polymer chain scission with the loss of mechanical properties. To combat this decomposition, hindered phenols are typically used as thermo-oxidative stabilizers. Such stabilizers act by deactivating PO_2^\bullet radicals by converting them to POOH and by inhibiting the hydrogen abstraction reaction (1) and the subsequent production of more PO_2^\bullet . For UV stabilization, hindered amine stabilizers are preferred as they may directly decompose PO_2^\bullet to inert by-products via a nitroxide intermediate in a catalytic process known as the Denisov cycle (Fig. 1) [7].

Hindered amine stabilizers (HAS) are commonly employed to protect agricultural film; however, there have been a number of reports on the negative effects of some agrichemicals on the efficacy of these stabilizers [4–7]. In polyolefin greenhouse applications, sulfur and chlorine-containing agrichemicals have been implicated in the suppression of activity of amine-type HAS due to chemical reactions of the acidic sulfur and chlorine-based compounds with the basic amine-type HAS. The ammonium salts produced in these reactions do not participate in the Denisov HAS stabilization cycle due to their inability to form the required nitroxide intermediate (Fig. 1). Instead, they remain as inactive compounds and reduce the overall effectiveness of the stabilizer in the film.

In contrast to the effects of agrichemicals on stabilizers used in polyethylene mulch film, the effects of agrichemicals on the degradation of polyethylene, itself, are largely unknown. The resistance of polyolefins to direct chemical attack and their environmental persistence suggest they should be inert, which is

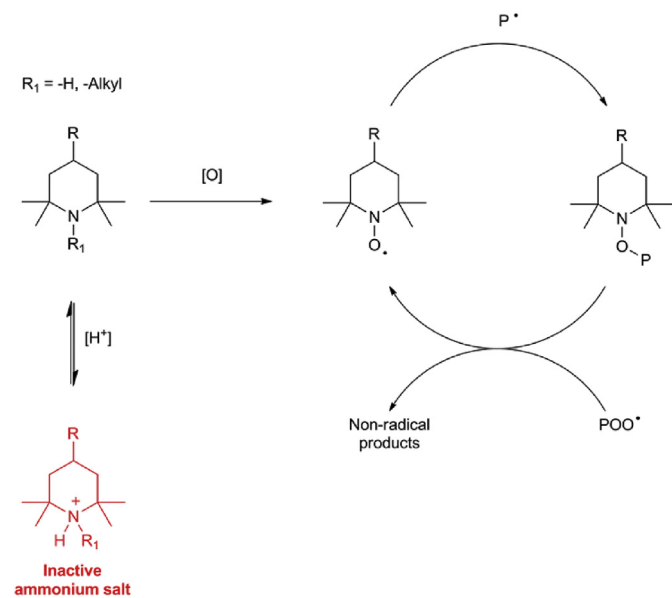


Fig. 1. A simplified Denisov cycle showing that an acidified hindered amine is inactive and cannot take part in the radical scavenging cycle. Amine-type HAS are alkaline and can form inactive ammonium salts with acidic compounds as shown on the left. Adapted from Refs. [7,11].

distinctly different from agrichemicals. Agrichemicals are required to degrade rapidly in the environment and are subject to a range of abiotic degradation processes, such as UV degradation, which affects their environmental impact [12]. During these degradation processes, intermediate species capable of initiating degradation in polyethylene may be formed. In particular, the photochemical activation of the commonly-used herbicide and well known violon, Paraquat (N,N'-dimethyl-4,4'-bipyridinium dichloride), generates free radicals such as superoxide [13–15], highly reactive species which may initiate degradation in polyethylene by consuming stabilizers and also potentially attacking the polymer. In addition, other agrichemicals, such as those based on dithiocarbamates which include the fungicide, Mancozeb, may potentially act as photo-prodegradants for polyethylene in the same way as deliberately engineered commercial degradable polyethylene film produced using a dithiocarbamate prodegradant technology developed by Scott and Gilead [8]. Therefore, the potential for agrichemicals to affect the degradation of polyethylene, beyond stabilizer inactivation and through direct initiation, is significant.

To study the effects of agrichemicals on the degradation of polyethylene films, a range of common agrichemical types was chosen: Paraquat (a herbicide), Sulfur and Mancozeb (fungicides) and Chlorpyrifos (an insecticide) (Fig. 2).

Both stabilized and unstabilized polyethylene films were studied in combination with individually-applied agrichemicals. The effects of these agrichemicals on the extent of oxidation of different types of polyethylene films under accelerated UV exposure are reported with the aim of differentiating effects due to stabilizer and intrinsic effects on the polymer.

2. Materials and methods

2.1. Materials

A resin blend was used to form a base polyethylene matrix which is suitable for agricultural applications as a clear thin film. This mixture comprised two different LLDPE resins (Dow Plastics, major co-monomer: 1-octene), a low amount of LDPE (Qenos) and PIB as a tackifier (Daelim Corporation, M_w 2000 g/mol).

A commercially-available white-on-black LLDPE-based polyethylene mulch film, containing an amine-type HAS stabilizer was also evaluated. The white layer of the film contained a rutile

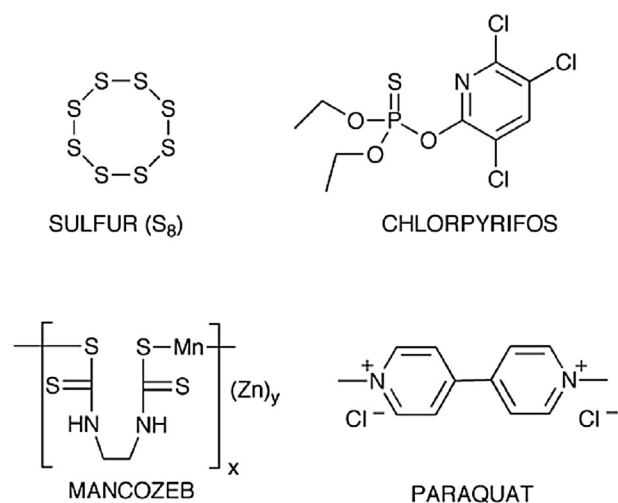


Fig. 2. Chemical structures of the agrichemicals used in this study.

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