

The Effect of Pesticides on the Degradation of Oxobiodegradable Agricultural Mulch Films

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Abstract

Oxobiodegradable agriculture mulch films made from polyethylene (PE) are known to have many benefits for agriculture practice, including increased yields and resource efficiency, without the drawback of removing the film after the growing season. However, anecdotal evidence suggested when pesticides are applied to these films, their rate of degradation may be affected. The goal of this investigation was to characterize the delay in degradation that occurs when pesticides are applied to oxobiodegradable agriculture mulch films. Two pesticides, Pyrinex 480 and Round Up, were tested in the field and laboratory environment to determine the effects on degradation with normal and accelerated exposure conditions for the films. Exposure tests indicated the pesticides were having stabilizing effects on the PE films, delaying degradation. Therefore, tests were designed to explore the chemical mechanisms underlying each pesticide's stabilizing influence. These included experimental and computational measurements of redox potential to define chain breaking donor and chain breaking acceptor capacities of the pesticides. UV (ultraviolet) screener capacity of the pesticides was also investigated. We concluded that Pyrinex 480 likely has the ability to absorb UV energy that would normally break bonds in PE, along with some other capacity to stabilize degradation, such as the ability to accept electrons. In contrast, Round Up likely donates electrons or atoms to prevent degradation reactions and stabilize PE films.

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List of Abbreviations

ATR.....	Attenuated Total Reflection
B3LYP	Becke3 Lee Yang Parr
BDE	Bond Dissociation Energy
DFT	Density Functional Theory
DSC	Differential Scanning Calorimetry
FTIR	Fourier Transform Infrared
HALS	Hindered Amine Light Stabilizer
PE	Polyethylene
Ra	Electroaccepting Index
Rd	Electrodonating Index
UV	Ultraviolet
UV-vis.....	Ultraviolet visible

Research Statement

The purpose of this thesis is to investigate the effects of pesticides on oxobiodegradable agricultural mulch films made from polyethylene. Although mulch may be used as a method of lowering or eliminating pesticide usage, pesticides and mulch are often used together for complementary effects. This leads to potential reactions between the mulch films and pesticides, possibly affecting the degradation of the films. Previously, pesticides were seen to affect stability of non-degradable agriculture mulch films made from polyethylene, but the reaction of pesticides with degradable polyethylene films has not yet been investigated.

This thesis aims to fill a gap in current polymer chemistry by comparing the effects of pesticides on the degradation of polyethylene mulch films. Fourier transform infrared spectroscopy is an ideal method for this analysis as it allows one to track the development of functional groups and bonds during degradation. It consists of five sections. Section one introduces the topic and reviews previous work. Section two describes the methods used. The results and a thorough discussion can be found in section three. Section four concludes this thesis and suggests future work. Appendices are included which contain supplementary information.

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Chapter 1. Introduction

In agriculture, unpredictable weather, predators and competition between annual crops and perennial weeds have and will always present problems that need to be overcome. With current population growth and climate change, agriculture will need to combat more challenges. These include lack of land for agriculture production despite an increased need for food, increased extreme weather, water scarcity and increased pest resilience with more strict guidelines for pest control¹. To address these issues, more sustainable agriculture practices need to be developed.

1.1 Sustainable Agriculture

Sustainable agriculture aims to overcome current and future problems of agriculture by increasing food production and decreasing required inputs². There are many different factors to consider for sustainable agriculture. Water usage needs to be decreased by preventing evapotranspiration and overwatering³. Using rain-fed watering systems can also decrease water demand. Managing and conserving soil is likewise important for sustainability. This can be approached by preventing erosion through reducing run off, planting crops that are harvested at different times, increasing ground cover and reducing tillage². All of these practices will prevent the gradual loss of arable land that routinely occurs from agriculture². Finally, investing in low input farming decreases the burden on the surrounding environment by reducing or eliminating additions such as pesticides and fertilizers².

Mulching is a method known to increase sustainability. Mulch is a layer of material over the soil that the crops can grow through and can be made of many different substances. The increased sustainability is due to a decrease in evapotranspiration, prevention of soil erosion and nutrient washout, decreased need for pesticides, and possible modification of the soil microenvironment⁴. Each of these benefits is dependent on the type of mulch used. The type of mulch also dictates whether it degrades or needs to be removed at the end of the growing season, which is another consideration for sustainability.

The earliest example of mulch is crops such as hay that were plentiful and applied in thick layers to suppress weeds and retain soil moisture⁵. This method of mulching is still used and is economical, but tends to cause weed seed transfer⁶. Paper mulches are also used and have the added benefit of warming the soil, but have a relatively high cost and poor durability⁵.

Aluminum foil has been applied as a mulch to control insect predation, but also has a high cost and may damage crops^{5,7}. Plastic mulch films were developed in the late 1930s and are inexpensive, have good durability, warm the soil, retain moisture and are resistant to degradation^{5,8-10}.

1.2 PE Mulch Films

Polyethylene (PE) is a type of synthetic polymer with many different methods of synthesis, depending on the desired properties of the film. It is classified into several categories with the most common three being low density PE (alkyl groups of various lengths on the polymer chain, some carbon-carbon double bonds), high density PE (lower chain branching, reduced toughness due to reduced amorphous phase), and linear low density PE (ethylene copolymerised with a small proportion of other alkyl-ethylenes)¹¹. Both low density and linear low density PE are commonly used for agricultural mulch films as they can withstand weathering

conditions, a result of the branching that occurs in the film creating strength in the machine direction^{12,13}. Low density PE is developed by free radical polymerization initiated by small amounts of oxygen or peroxides at temperatures up to 350 °C and pressures between 15 000 and 50 000 psi¹³. In low density PE there are between four and 15 short alkyl chain branches in every hundred carbon atoms limiting the crystallinity of low density PE to about 50 %¹³. Linear low density PE does not contain the long branches in low density PE and is formed from gas-phase copolymerisation of ethylene with small amounts of higher 1-alkenes¹³. It can be produced at much lower temperatures and pressures than low density PE¹³. The lack of long branches in linear low density PE gives better resistance to tensile strain compared to low density as the chains in the polymer do not get entangled during elongation¹³.

Figure 1.1 shows an example of a small scale plastic mulch agriculture system.



Figure 1-1: PE films being used to grow corn, sweet peppers and tomatoes.

PE film can be prepared in a variety of colours. The colours are used to obtain a specific microenvironment for the crop being grown through modifying root zone temperature, reflected

light and pests¹⁴. PE films are relatively inert in pure form which is advantageous because they will not degrade, giving the plants adequate protection during growth¹¹. Additionally, opaque films block light from reaching anything other than the desired crop, decreasing weed production without the application of pesticides¹⁵⁻¹⁸. PE films may cause an increase in yields and growing season length when compared to bare soil¹⁵⁻¹⁸.

While PE films have many positive impacts in agriculture they lack susceptibility to degradation because the composition begins as large macromolecules that cannot be consumed by microorganisms^{8,9,15,19-22}. The film must therefore be removed and disposed of at the end of the season, adding a cost of approximately \$250 /ha²³. The waste is a substantial consideration since plastic mulches are sold by the hundreds of thousand pounds in Europe every year with amounts increasing elsewhere in the world²⁴. Eliminating the waste problem of the films, along with the cost of removal and disposal, can be achieved through controlled degradation of PE. An ideal degradable PE film will protect the crops until a short period prior to harvesting, allowing the crops to grow without competition from weeds and reap the temperature benefits associated with plastic mulch. Prior to harvesting the film will then degrade quickly, losing strength that could cause damage to the crops or machinery at the end of the season. Any unpredictable changes in film degradation may expose the plant too early to environmental hazards stunting growth or impair harvesting.

1.3 PE Degradation

To be considered a degradable plastic, the ASTM specification relating to plastics (D883-12) stipulates that a plastic has to undergo significant changes in its chemical structure under specified conditions that result in a loss of properties²⁵. In regards to PE mulch film, the carbon-

carbon backbone of the chain needs to break down under conditions typically found in agriculture environments. Pure PE is not readily susceptible to degradation because PE consists of repeated ethane units and lacks functional groups (figure 1-2).

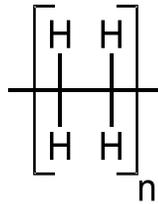


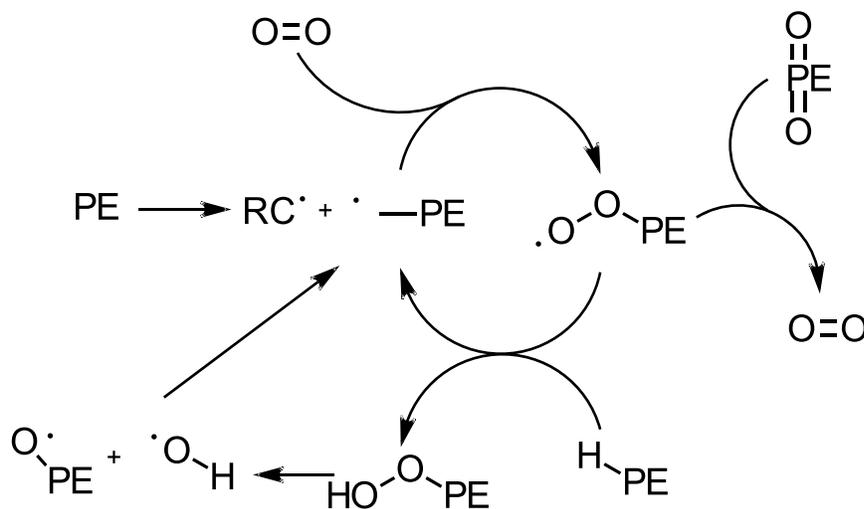
Figure 1-2: Structure of pure PE.

However, manufactured PE has impurities introduced into its structure during processing at high temperatures and pressures²⁶⁻²⁸. These impurities will cause PE to break down within weeks of outdoor exposure. The lower molecular weight units can then undergo biodegradation, with the process varying from hours to years depending on the nature of the functional groups²⁹. Biodegradation is the breakdown of organic materials into smaller compounds via metabolic or enzymatic processes.

There are multiple factors that can affect how quickly the degradation of PE used for mulch films occurs, including exposure to sunlight, oxygen, water, mechanical stress, living organisms and pollutants³⁰. The amount of sunlight that reaches the film is influenced by the crops being grown, and all of the above factors are affected by geography and season⁷.

The initial breakage of bonds will allow the incorporation of oxygen into PE. This is referred to as the initiation step and can occur in several ways. Photo-oxidative degradation involves the polymer absorbing ultraviolet light. Thermo-oxidative degradation involves the breakage of bonds from heat exposure. Mechanical stress can also affect degradation through strain occurring on the different bonds¹⁰.

Initiation results in the formation of free radicals and increases the amount of functional groups as seen in scheme 1-1. Any method that causes free radicals can be referred to as an initiation step. As a result of environment variability and initiation processes, the degradation of these films involves several degradation mechanisms occurring at once³¹. Regardless of the source of initiation, however, hydroperoxide or ketone groups are the primary oxidation products. Hydroperoxides are thermally and photolytically unstable and are further decomposed by both heat and light^{10,32}. Ketones can only be further decomposed by light³³. If the reaction mechanism results in more ketone production heat will not play a major role in breaking down the film but light exposure will.



Scheme 1-1: Overall mechanism of PE degradation. Adapted from reference 34.

Once the initiation reaction(s) have occurred propagations continue on by auto-oxidation cycles which are common in all polymers with a carbon backbone (scheme 1-1)^{19,35,36}. The occurrence of propagation depends on the free radical chain reactions of the polymer with oxygen and/or how easily hydrogen can be removed from the backbone. Propagation will continue throughout the chain until a species terminates the reaction (scheme 1-1). There are

many methods of chain termination, all involving the stabilization of free radicals. For detailed mechanisms regarding initiation, propagation and termination refer to Appendix I.

As polymers need to maintain their properties for what is often a roughly-defined length of time before they degrade, the propagation cycle may need to be delayed. This is achieved through the use of stabilizers. For films that are meant to degrade, these stabilizers are counteracted by prodegradants after the polymer has finished the timeframe for the expected service life. The prodegradants encourage the incorporation of oxygen into the polymer. For more information on additives see section 1.4 and Appendix I.

1.3.1 Photo-oxidative Degradation

Photo-oxidative degradation involves polymers undergoing reactions with oxygen found in the atmosphere when exposed to light. The bond dissociation energy (BDE) of carbon-carbon and carbon-hydrogen bonds (the two bonds in pure PE) are 375 kJ/mol and 420 kJ/mol respectively³⁷. Ultraviolet (UV) light between 290 and 400 nm (UVA and UVB) light has energies between 412 kJ/mol and 300 kJ/mol, respectively. Therefore, direct photolysis of the carbon-carbon bond may result in radical formation that will propagate throughout the polymer chain. However, the photolysis of carbon-hydrogen bonds is considered unlikely because of the higher associated energy^{10,37-40}. Nevertheless, functional groups and points of unsaturation occurring in PE from processing have lower energy requirements for bond breakage (e.g. hydroperoxide can have bond energies as low as 180 kJ/mol)^{37,41}. These areas are sources of attack for oxygen, resulting in chain oxidation and oxygen-oxygen bond formation that can take part in many cycles of initiation¹⁹. It should be noted, however, that photo-oxidation is limited by diffusion of oxygen, as the inner layers cannot always be reached, and is therefore more prominent on the surface of PE films.

1.3.2 Thermo-oxidative Degradation

Thermo-oxidative degradation may occur during polymerization, storage, molding, and service life³⁶. There are two distinct reactions that can occur when a polymer is exposed to heat. One is random scission of links which occurs where functional groups are incorporated in the chain and results in molecular weight loss¹⁹. The other is chain end scission (unzipping) of carbon-carbon bonds generating volatile products of one or two carbons¹⁹. Thermo-oxidation is not limited to the outer layers and the rate increases with temperature^{10,42,43}.

1.3.3 Mechanical Degradation

Mechanical degradation is an important consideration. When mulch films are applied to a soil surface they must be applied tightly and as close as possible to prevent any hot air that may become trapped underneath the film from damaging crops⁵. The tight application also allows heat conduction from the plastic to the soil⁴⁴. Applying mechanical stress to a polymer can accelerate the degradation because both photo- and thermo-oxidative degradation are morphology-dependant¹⁰. The morphological changes include the straightening of polymer chains which results in easier cleavage due to increased strain and more distance between radicals making them less likely to recombine¹⁹. The distance between radicals is increased because the strain stretches the different chains of the PE. Mechanical stress may also cause bond scission and/or slippage of chains³⁸.

1.3.4 Biodegradation

It is important to distinguish between oxodegradation, which results in deterioration of mechanical or other physical properties, and biodegradation, which is the transformation of material to carbon dioxide, water and biomass from microbe assimilation⁴⁵. These two types of degradation are dependent on each other, although they are two distinct steps. The first step is

abiotic and breaks the long chain into oligomers and monomers^{10,19,46,47}. The second step is biotic, and results in the microorganisms assimilating the oligomers and monomers^{10,19,47}. The first step is “rate-determining” for these reactions and therefore the focus of this thesis, as biodegradation will not occur if the oxygen is not incorporated into the chain^{1,10,27}.

Although the focus of this project is not on biodegradation, it is still important to know the requirements of PE oxodegradation that will allow biodegradation to proceed. After fragmentation of the polymer chain the low molecular weight oxidation products are readily consumed by microorganisms. There are some conflicting results on how low the molecular weight has to be in order to be accessible to the bio-organisms. Previously, a study indicated n-alkanes of up to 500 Da can be decomposed⁴⁸. More recently, however, other studies have reported that longer alkanes are bioavailable^{19,45}.

1.4 Oxobiodegradable PE and Additives

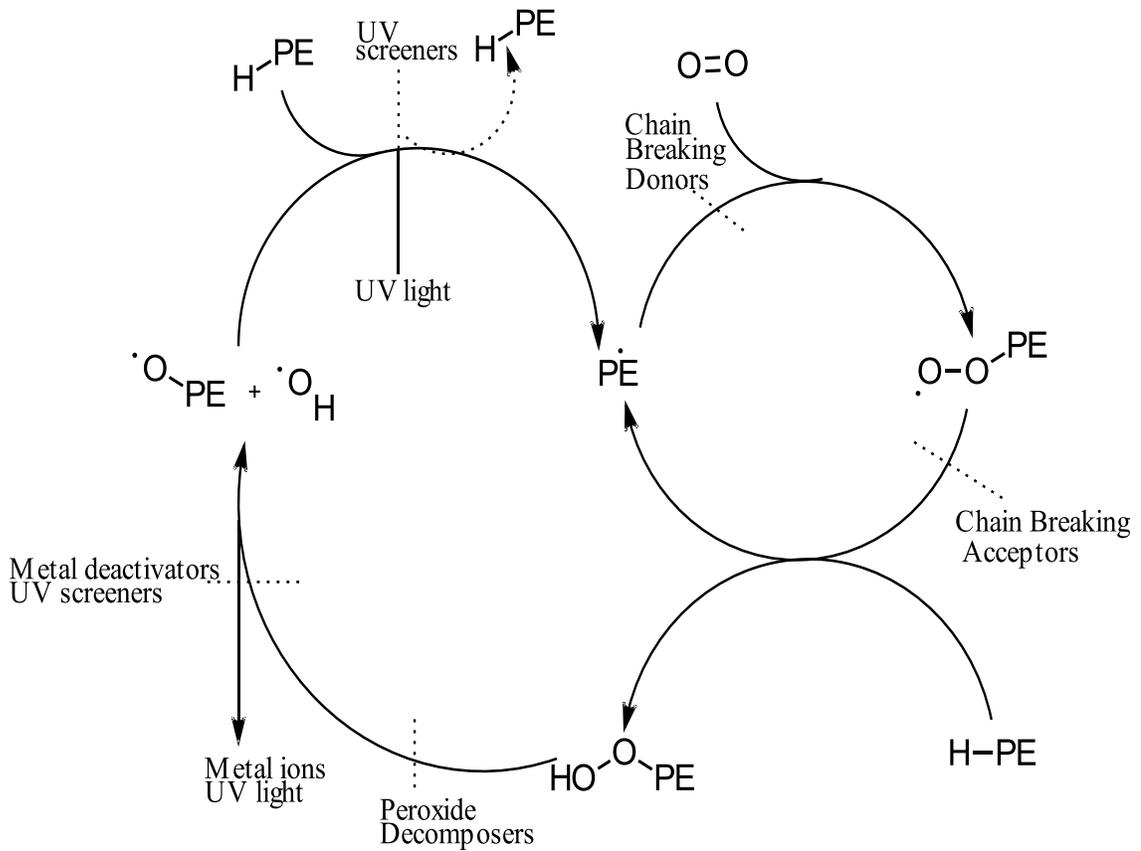
Making PE oxobiodegradable requires additives to keep the film stable for the desired lifetime combined with additives to make the film breakdown shortly after the lifetime has expired. There are three main types of additives in PE relating to oxobiodegradable agricultural mulch films: stabilizers, prodegradants and fillers.

1.4.1 Stabilizers

Without the addition of stabilizers any PE mulch film will only last a few months, with a constant decline in physical properties over time. This is a result of oxygen containing functional groups (e.g. carboxylic acids, hydroperoxides etc.) that occur in the PE chain during processing⁴⁹. Stabilizers can be classified into five main types and are designed to prevent chemical reactions from occurring in the film: a) Screeners/absorbers prevent UV absorption or

reflection³⁴; b) Chain-breaking donors donate electrons or atoms which inhibit propagation³⁴; c) Chain-breaking acceptors inhibit propagation by accepting electrons or atoms³⁴; d) Peroxide decomposers break down hydroperoxide without creating free radicals³⁴; and e) Metal deactivators inhibit propagation reactions caused by metal impurities present in the film^{34,50}.

Any stabilizer has a time dependence associated with its concentration and it will eventually be consumed. This cannot be ignored when predicting degradation⁵¹. The ways in which stabilizers may affect PE degradation are represented in scheme 1-2.



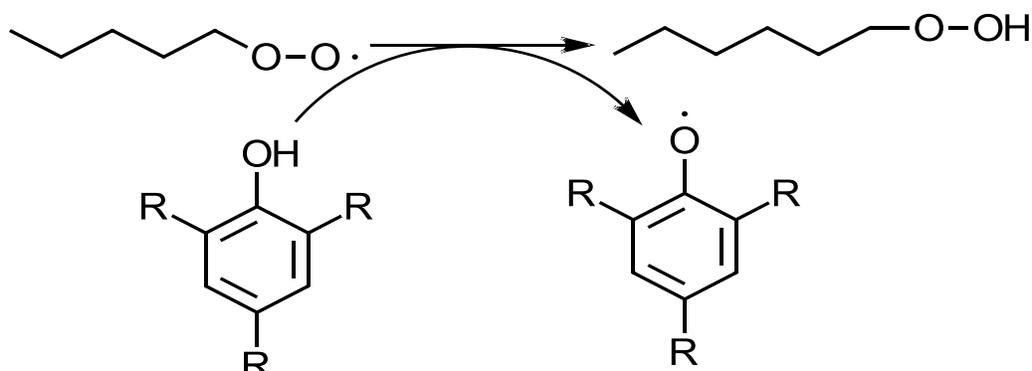
Scheme 1-2: Different degradation mechanisms of PE, indicating by dashed lines where stabilizers can affect degradation. Adapted from reference 34.

1.4.1.1 Ultraviolet Screeners

Many different molecules can act as UV screeners. If a molecule absorbs or reflects UV light it can potentially act as a screener because the UV light will be dispersed from the polymer. UV screeners rarely only act by absorbing or reflecting UV and often have additional stabilizer capacity³⁴. An example of a reaction a UV stabilizer may undergo is found in Appendix I-4.

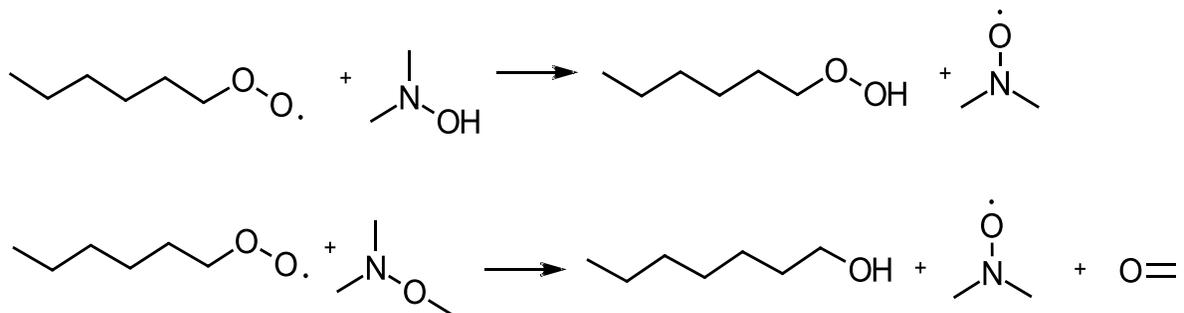
1.4.1.2 Chain Breaking Donors

The main classes of chain breaking donors are aromatic amines and phenols, with phenols being the main stabilizers for plastics⁵². These stabilizers donate a hydrogen atom to the free radical, preventing further propagation of the radical (Scheme 1-3)⁵³.



Scheme 1-3: Simple example of stabilization by a chain breaking donor. The radical in the donor is subsequently stabilized through resonance and/or steric hindrance or two donors will stabilize each other. Adapted from reference 53.

Hindered amine light stabilizers (HALS) are widely used as free radical scavengers⁵⁴. They are good photo stabilizers (even though they do not absorb UV light) and react through the generation of a nitroxide from the parent amine (Scheme 1-4), which scavenges alkyl and acyl radicals⁵⁵. HALS may also hinder propagation in the beginning of oxidation through peroxy compound reactions and complex impurities of trace metal ions⁵⁵.



Scheme 1-4: Reactions typical of hindered amine stabilizers. The formed amine radical can then take part in secondary reactions. Adapted from reference 52.

Photostable phenolic stabilizers often have substitution occurring at position four (para) to increase the stabilization of the phenol, but are known to be of limited effect in environments with high temperatures and pressures^{55,56}. Hindered phenols have been shown to be effective long-term heat stabilizers, acting as radical scavengers by transferring the hydrogen atom from the phenoxyl group of the stabilizer to a peroxy radical resulting in hydroperoxides⁵³. The stability and reactivity of phenoxyls is then determined by steric effects on substituents at the ortho or para position on the phenol as well as by the extent of delocalization of the unpaired electron⁵⁷. If phenolic antioxidants are used, there is usually a well-defined induction period with little to no activity, followed by rapid degradation⁵². The quick degradation occurs because there are no longer any molecules preventing free radicals from propagating through the film. Also, the stabilizers create hydroperoxides which can break down leading to other degradation products.

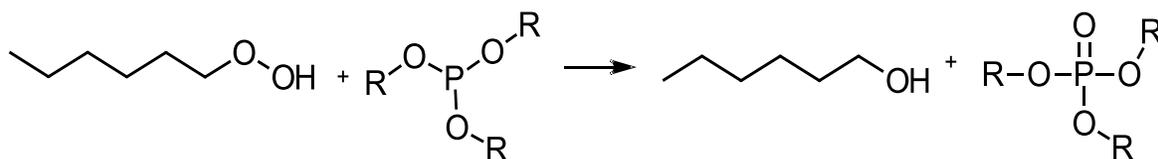
1.4.1.3 Chain Breaking Acceptors

Chain breaking acceptors are known to inhibit free radicals because of their ability to be reduced. Different electron attracting groups such as halogens increase the accepting capacity,

where electron releasing groups such as alkanes decrease the accepting capacity. Common acceptors include phenoxyls, quinones and semiquinones, and nitroxyls all which experience stability from resonance³⁴.

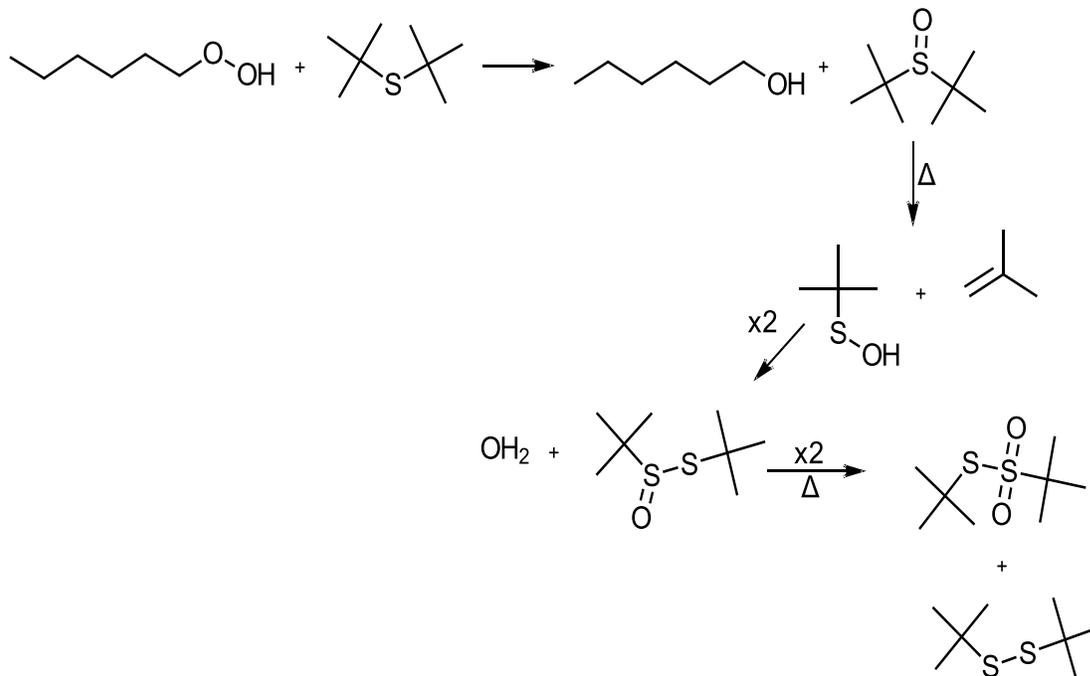
1.4.1.4 Peroxide Decomposers

Peroxide decomposers breakdown hydroperoxides without allowing the formation of free radicals¹¹. Aryl phosphites are one type and can be used as stabilizers during the melt processing of polyolefins. The reaction of these molecules relies on the phosphite being oxidized into phosphate through reducing hydroperoxides (Scheme 1-5)⁵⁸.



Scheme 1-5: Phosphites decompose hydroperoxides. Adapted from reference 34.

Organic thiocompounds are another commonly used peroxide decomposer. They are often used in blends with phenols, supporting the phenolic scavenging of RO_2^* and non-radical deactivation of RO_2H , where R represents the PE chain (Scheme 1-6)⁵⁹.



Scheme 1-6: Sulphides inhibit reactions by preventing further reactions. They are not initially stabilizers, but become stabilizers during autoxidation. Adapted from reference 34.

1.4.1.5 Metal Deactivators

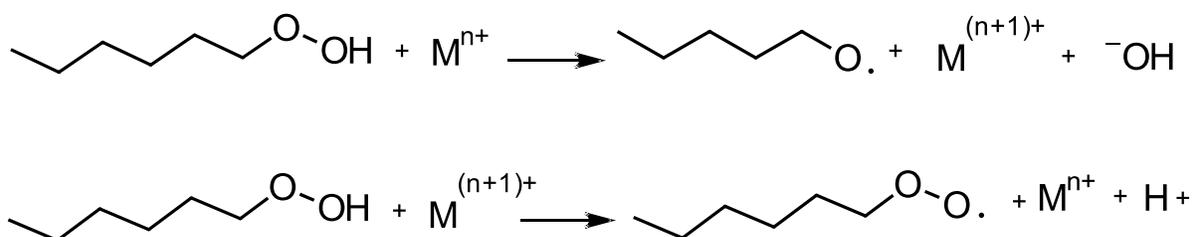
Metal deactivators are specific species incorporated into the film to prevent metals from promoting degradation. They are responsible for two different processes: removing prooxidant transition metal ions from hydroperoxide proximity and deactivating the metal through saturation of the metals outer coordination shell³⁴. Amines and molecules containing sulphur have been seen to act as effective metal deactivators^{34,60}.

1.4.2 *Prodegradants*

Prodegradants are an important addition to oxobiodegradable films to make sure that, once the stabilizers are consumed, the plastics degrade quickly. They have been employed for over three decades to eliminate some of the waste problems associated with plastics⁶¹. The prodegradants are usually added into the final polymer formula, in small levels, as a means of

increasing the speed of oxidation¹⁵. Once PE has begun to degrade and hydroperoxides are formed they are reduced by the prodegradant, usually transition metal ions²⁸. This reduced species then undergoes further propagations.

The most commonly used metals are iron, cobalt and manganese or other transition metals. Transition metals can easily transfer between two oxidation states (Scheme 1-7), as the metal gives or receives an electron, which promotes the transfer of free radicals throughout the polymer⁹. As the metal changes between the oxidation states easily small amounts of the metal have a very large effect as a prodegradant⁹.



Scheme 1-7: Redox reactions in the PE structure where M represents a transition metal prodegradant. Adapted from reference 9.

Often the use of heavy metals as prodegradants leads to concerns of accumulation of the metals in the environment, or bioaccumulation. Preliminary studies on nickel and cobalt dithiocarbamates indicated that the likelihood of these prodegradants environmentally impacting the soil is very low because of undetectable additions of the metal (to the soil)⁶². Other prodegradants include manganese, iron and copper, which are micronutrients for crop development and are therefore needed in the soil. However, at the present time, there is not enough research to confirm that there will be no bioaccumulation for the crops and it is therefore important to keep this in consideration.

There are a variety of other additives that have been used as prodegradants. Some of the most common include organic compounds incorporating carbonyl groups and conjugated double bonds, metal oxides, and sulphur ligands with metal ions. Overall these prodegradants have the disadvantage of decreased control over the degradation time and low selectivity resulting in side reactions.

1.4.3 Fillers

Fillers are used in plastics for many different purposes. Carbon black is one example of an important filler that has an impact on degradation. The addition of carbon black in high concentrations (around 30 %) can be used to increase UV stability, although carbon black has occasionally been reported to initiate decomposition in the films if there is high volatile content⁶³. The film used in this study is clear and therefore has no carbon black in its structure.

Although there are other fillers that can be included in PE materials (fire retardants, lustre additives etc.) they will not be considered in this study.

1.5 Pesticides and Plastic Mulch Film

Despite the call for more sustainable agriculture and therefore the decrease of pesticides, these chemicals are still relied upon for profitable farming⁶⁴. Pesticides have many reactions associated with them and as such can influence materials they come into contact with. They may be added intentionally in order to ensure protection from weeds and insects or accidentally (for example, through contamination of the film from pesticide applied in close proximity). It is therefore important to consider any effects that pesticides may have on oxodegradable mulch films. Just as additives that have defined purposes in the films cause reactions, the addition of pesticides to the films may provoke or prevent chemical reactions.

The most commonly used pesticides may be divided into two categories: herbicides and insecticides. Agriculture fields that are covered in opaque PE mulch have decreased herbicide need because light that would normally reach the weeds is blocked. However, herbicides are often used in combination with mulch to increase resistance to weeds, especially those which are not controlled by mulch (e.g. purple and yellow nutsedge)⁵. Also, if clear PE is being used, the light is not blocked from the weeds resulting in the requirement of herbicide as a method of weed control^{7,17,65}. Although some studies have noted that insects may become confused and less persistent when mulch is used⁷, insecticides may be required nonetheless.

It has been reported that pesticides remain active on plastic mulch film 120 hours following their application⁶⁶. Another study showed that all pesticides considered herein were absorbed into the films slowly and remained chemically stable⁶⁷. Therefore it is known that pesticides can remain on the film long after application.

There has been little research done involving pesticides and oxodegradation. A study on the capacity of antioxidants in non-degradable PE mulch films and pesticide application showed that pesticides containing copper, carbamate, and thiocarbamate decreased the stability of the film against oxidation and pesticides with sulphur increased the stability of the film against oxidation⁶⁸. The researches stated that this was unsurprising as sulphur and sulphurous compounds are known to act as stabilizers categorized as peroxide decomposes through decomposing hydroperoxides⁶⁸.

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Chapter 2. Methods

2.1 Objectives

There are a variety of different types of pesticides. To be pertinent to Canadian farmers and agriculture research, the top 20 pesticides used in Canada in 2005 were considered for the present study. Of these 20 pesticides, five are not typically applied to an agriculture field (i.e. normally used with trees)¹. Of the remaining 15 pesticides, two were studied in experimentally and all 15 were studied computationally (Appendix II).

The two pesticides studied in the laboratory were Pyrinex 480 and Round Up and their active ingredients chlorpyrifos and glyphosate, respectively, are represented in figures 2-1 and 2-2.

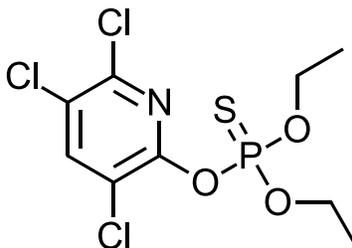


Figure 2-1: Chlorpyrifos, the active ingredient in Pyrinex 480.

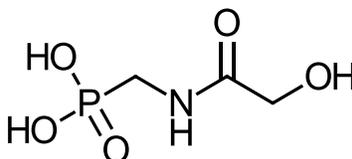


Figure 2-2: Glyphosate, the active ingredient in Round Up.

Determining if the pesticides have an effect on degradable mulch requires comparing the degradation of films with applied pesticides to the degradation of film with the same composition

without applied pesticide. Measuring the change in degradation in photo and thermal accelerated environments can lead to suggestions of what effect the pesticides have on the films.

2.2 Materials

The film used in this study was clear PE film with a thickness of 7.5 μm . The film was linear low density PE with a copolymer of octene manufactured with gas phase technology using a titanium base catalyst with a co-catalyst of aluminum and magnesium. The antioxidants present in the film were a blend of phenolic and phosphite (at a concentration between 500 and 5 000 ppm) and a talc antiblock (at a concentration between 1 000 and 5 000 ppm). The film also contained a UV stabilizer at a concentration of 100 to 6 000 ppm, a slip additive of euraamide or oleamide at a concentration in between 400 and 3 500 ppm and finally a blend of agricultural macro and micronutrients consisting of one or more of the following: calcium, magnesium, iron, manganese, copper, boron, molybdate, and/ or zinc, as an oxide, chelate or carboxylate form at concentrations from 10 to 1 000 ppm. These films were exposed in the SEPAP and oven using holders to consistently measure the same area in FTIR. Because all of the films used were assumed to be nominally identical with respect to the contained additives, any difference measured between untreated films and those dosed with pesticides were interpreted as resulting from the pesticides themselves or interaction between the pesticides and PE. Any synergistic effects that might arise because of interaction between the pesticides and additives in the film were not considered. Further testing that includes films or models systems without the presence of additives may validate this approach to interpretation of the results.

Pyrinex 480 and Round Up were of commercial grade. The Pyrinex 480 contained chlorpyrifos as the active ingredient and kerosene as the solvent whereas Round Up contained isopropylamine salt of glyphosate. The chemicals used in the laboratory experiments included

ammonium molybdate (4 mM, 99.98 % purity), caffeine (0.05 g/L, 99 % purity), citric acid (0.05 g/L, 99.5% purity), ferrous ammonium sulphate (0.2 mM, 98.5 % purity), ferrozine (5 mM, 98 % purity), sodium phosphate (28 mM, 99 % purity) and sulphuric acid (0.6 M, 95-98 % purity).

2.3 Degradation Measurements

2.3.1 Theory

Due to the simple structural differences between non-degraded PE and degraded PE, Fourier transform infrared spectroscopy (FTIR) is an ideal method for tracking the change associated with degradation over time. Degradation in PE is known to occur when oxygen is incorporated into the film and, therefore, the amount of functional groups containing oxygen, such as ketones and carboxylic acids, will increase. FTIR can be used to track the increase in oxygen containing functional groups in PE.

In FTIR, a source of infrared radiation is split into two beams by the Michelson interferometer, which is basically a system of moving and fixed mirrors². The two beams are passed through the sample creating an interference pattern². The interference patterns allows a calculation of absorbance versus time and all frequencies are measured at one time making it much quicker than dispersive IR spectroscopy². The interference pattern that reaches the detector can be Fourier transformed from a time based wave signal into frequency components². Peaks occur in IR absorption spectra because of bond vibrations. The frequency and intensity of the peaks indicate the strength of the bond in the molecules, mass of the atoms in the bonds, number of molecules with the same functional groups, dipole presence, and type of vibration². Spectral “noise” can be minimized by making multiple scans of the same sample and averaging the scans².

FTIR spectroscopy is commonly cited throughout the literature as a method of measuring the degradation of polymers³⁻²². This is due to the ease with which a variety of chemical changes associated with the degradation of PE (table 2-1) can be monitored and the fact that it is a non-destructive technique. The level of oxidation can be affected by a variety of interacting parameters, such as intensity of sunlight, length of exposure to light and oxygen and type of additives¹³. The increase of carbonyl groups and other points of unsaturation in PE indicate that oxidation has taken place and the material is vulnerable to further degradation⁸. Most of these oxidation products have characteristic absorption peaks between 1850 cm⁻¹ and 1700 cm⁻¹, which represent the C=O stretching vibration of carboxylic acids, aldehydes, esters, and ketones²³ (table 2-1).

Table 2-1: FTIR peaks analyzed to characterize PE degradation.

Wavenumber cm ⁻¹	Functional Group	Expected Trend with Increasing Degradation
3370	hydroxyl ²²	Weak increase in peak height
3350	hydroperoxide ²⁴	Medium increase in peak height
1785	cyclic ester ^{7,25}	Strong increase in peak height
1740	acyclic ester ^{7,26}	Strong increase in peak height
1730	aldehyde ²⁶	Strong increase in peak height
1720/1715	ketone ^{7,26,27}	Strong increase in peak height
1715/1185	carboxylic acid ^{7,27}	Strong increase in peak height
1640	carbon-carbon double bonds in the middle of the chain ³	Medium increase in peak height
1575	carboxylate ²⁸	Weak increase in peak height
1463	methylene scissoring ²³	No significant change in peak
915	carbon-carbon double bonds at the end of the chain ^{3,27}	Weak increase in peak height
888	trans-vinyl ^{22,27}	Weak increase in peak height
722	methylene rocking ²³	No significant change in peak

Expected increases in peak heights found in table 2-1 are from the associated functional groups containing oxygen or unsaturation. Prior to the film being exposed to factors causing

degradation there should be very small amounts of oxygen and/or unsaturation in the polymer chain. The small amounts that may be present are a result of the high heat and pressure during processing. During degradation oxygen is incorporated into the film which will result in functional groups with a range of stability. Peaks corresponding to ionic functional groups such as hydroxyl and carboxylate are expected to increase in height less than others. Those corresponding to functional groups with some stability but susceptible to propagation, such as hydroperoxides, are expected to have peak height increases stronger than functional groups containing ions. This is due to a suspected higher concentration of these groups compared to ionic functional groups because of increased stability. Peaks associated with functional groups with the highest stability in degradable PE, such as ketones, are expected to have the highest increase in height as they will participate in less propagation reactions and remain in the film longer.

Wavenumbers associated with bonds that are not expected to change from degradation have all been measured as a reference. Using FTIR to measure PE degradation requires a reference measurement because even under controlled environments for manufacturing PE films, the thickness of the film will change depending on where the sample is measured. This difference in thickness becomes more pronounced as degradation occurs. Using a peak that is known to not significantly change during degradation as an internal reference allows the comparison of different films regardless of functional group composition and thickness.

The carbonyl index is the most commonly cited indicator of PE degradation and is calculated by dividing the maximum amplitude in the 1715 cm^{-1} region by the amplitude of the methylene scissoring peak^{4-6,8,11-13,15,16,18-21} centred at 1463 cm^{-1} , which should remain stable during degradation. The peak at 1715 cm^{-1} is commonly used because it increases as a result of

most of the different oxidation products that occur during degradation giving an approximation of the total oxidation.

2.3.2 Method

Three replicas of film were exposed in the SEPAP (12/24, ATLAS Materials Testing Solutions), a photo-accelerating device that exposes samples to UVA and UVB (wavelengths ranging from approximately 290 to 580 nm) light at an intensity of 80-100 W/m². Samples were exposed at 60 °C for a total of 35 hours at which time the samples had begun to fragment, indicating that degradation had occurred. Samples were analyzed using a ThermoScientific Nicolet 6700 FTIR set at a resolution of 4 cm⁻¹ and taking an average of 32 scans of each sample after 5, 15, 21, 28 and 35 hours of exposure in the SEPAP device. Both peak amplitude and peak area were measured as a function of time and plotted to determine data consistency.

Despite being the most common measurement of PE degradation in the literature, measuring the maximum amplitude of the peaks in the 1715 cm⁻¹ area was not ideal because it did not allow determination of which functional groups were occurring. However, area measurements resulted in ambiguity in the results when the entire carbonyl area was measured after normalizing and when the overlapping peaks were deconvoluted. Deconvolutions were performed in the 1715 cm⁻¹ area using PeakFit with a Gaussian – Logarithm method with self-deconvolution based on the maximum height of peaks found in the literature^{7,25-27}. The best baseline (linear) option was used and only fits of R² > 0.9990 were accepted for all deconvolutions. After consideration of both the peak height and peak area, the peak height was chosen as the measurement of degradation. For all measurements of degradation the time of degradation was taken as the last measurement made before the film completely fragmented and therefore could no longer be measured using FTIR.

2.4 Pesticides and Plastic Mulch Films

2.4.1 Theory

When pesticides are applied to agriculture mulch film only one side of the mulch film will typically be treated. Therefore, it is significant to know whether or not the pesticide is staying on the top of the film or migrating through and affecting the entire sample. Also, the presence of pesticide will give rise to additional FTIR peaks. It is therefore prudent to determine peaks of the pesticide being analyzed and to compare these peaks to PE. If the peaks of the pesticide and PE do overlap it would be assumed that FTIR analysis of degrading PE with applied pesticides would give inaccurate results. To determine whether there was interference between the absorption of the pesticides considered and PE in FTIR, measurement of the spectra of the pesticide alone, the PE film alone and the PE film with pesticides applied were made.

Attenuated total reflectance (ATR) Fourier transform infrared spectroscopy is a surface-sensitive technique that can be applied to measure the difference (if any) between the top and the bottom of the film. This allows a comparison between what functional groups are occurring where the pesticide was and was not applied. In ATR, the spectra are measured through a totally internally reflected infrared beam²⁹. This beam is directed onto an optically dense crystal with a high refractive index at a specific angle²⁹. Total internal reflectance creates an evanescent wave that extends beyond the crystal's surface into the sample, which is held in contact with the crystal²⁹. If the sample absorbs energy, the wave is attenuated as it passes to the detector²⁹. The evanescent wave has limited penetration of the sample, approximately 1 μm , making it sensitive only to the sample surface²⁹. This method allows more specific sample measurement that makes possible differentiation between the top and bottom film surface (while transmission averages over the entire sample thickness).

Assuming the pesticides do affect the oxobiodegradable films, the difference between the top and the bottom of the film is important because it may suggest a possible means by which the PE is affected. For example, one type of stabilizer, UV screener, is known to prevent photo-oxidation degradation. Since photo-oxidative degradation is mostly limited to the surface of the film (section 1.3.1), a higher amount of pesticide on the top of the films may indicate a capacity of the pesticide to act as a UV screener.

Previous analysis of pesticides added to non-degradable PE films indicated UV absorbance measurements of the film may predict if the pesticide will affect the films' degradation. The study showed when films were exposed to pesticides that did not affect the stability of the stabilizer in the films the UV spectra changed slightly, if at all³⁰. On the other hand, pesticides which exhibit intermediate interactions with the stabilizer changed the intensity of UV absorption bands without causing a peak shift³⁰. Lastly pesticides with strong interactions with the stabilizer changed both intensity and peak position for the PE scan³⁰. Although the changes in UV absorption can indicate if the antioxidants are interacting with the pesticides, UV absorption does not provide insight into the manner in which these species are reacting.

2.4.2 Method

ATR spectra of the pesticides were measured to determine if any of the peaks corresponding to the pesticide matched those of PE. A ThermoScientific Nicolet 6700 FTIR set at a resolution of 4 cm⁻¹ was used. The FTIR was fitted with a MIRacle ATR attachment (Pike Technologies, WI, USA) using a diamond-covered ZnSe single reflection window. 32 scans were averaged for each measurement.

To determine if the pesticide was migrating into the film, ATR scans of the PE film were measured before and after pesticide application (table 2-2). Both the exposed and unexposed

sides of the film were measured. Scans were replicated three times. Pesticides were applied to the film in a four-walled apparatus. The film and apparatus were measured separately, pesticide was sprayed on the film, and the film and apparatus were continually measured until the mass of the film was stable. The films were also measured using UV-vis spectroscopy, as a previous study indicated this may be a method of predicting how pesticides may affect PE films³⁰. UV spectra were recorded for each film one hour, two days, one week, two weeks, and one month after dosing. All measurements were replicated three times.

Table 2-2: Samples with applied pesticide for ATR and UV scans.

Film with 0.0066 ± 0.0005 g of Pynex 480 per m ² of film
Film with 0.0261 ± 0.0005 g of Round Up per m ² of film

2.4.3 Exposure Environments

To measure the degradation of PE it is important to make sure the exposure is representative of the conditions that the PE will be used for. Therefore, field data is required to ensure all the film is exposed to environmental factors that may occur during usage. However, as there are many different variables in the field it is hard to specify what is occurring. Therefore, tests that simulate both accelerated UV exposure and accelerated thermal exposure are important to determine the influence that a pesticide may have and its mechanism of action.

2.4.3.1 Field

During the 2014 growing season, a plot was prepared on the outskirts of Oro-Medonte (44.622570, -79.698582). This plot consisted of five squares that were 30 cm wide and 75 cm long. Each square contained a film either with or without applied pesticide (table 2-3). Films were dosed by spraying with pesticides diluted to 2.84 g/L, and the amount applied to the film was calculated by measuring the spray bottle mass before and after pesticide application (table 2-

3). Every week for nine weeks two small squares (of area approximately 4 cm²) were cut from each film sample, and analyzed using FTIR in transmission mode.

Table 2-3: Field set-up exploring the difference in degradation with applied pesticide.

Blank film	Film with Round Up (I) 0.0024 g ± 0.0005 g /m ²	Film with Round Up (II) 0.0048 g ± 0.0005 g /m ²	Film with Pyrinex 480 (I) 0.0029 g ± 0.0005 g /m ²	Film with Pyrinex 480 (II) 0.0061 g ± 0.0005 g /m ²
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2.4.3.2 SEPAP

Accelerated testing of photo-oxidative degradation occurred in the SEPAP 12/24, which does not isolate photo from thermal effects. The SEPAP 12/24 device was held at 60 ± 4 °C. The SEPAP exposes the samples by a carousel sample holder in the middle of the device that constantly rotates during testing. The device exposes the samples to a variety of wavelengths as shown in figure 2-3.

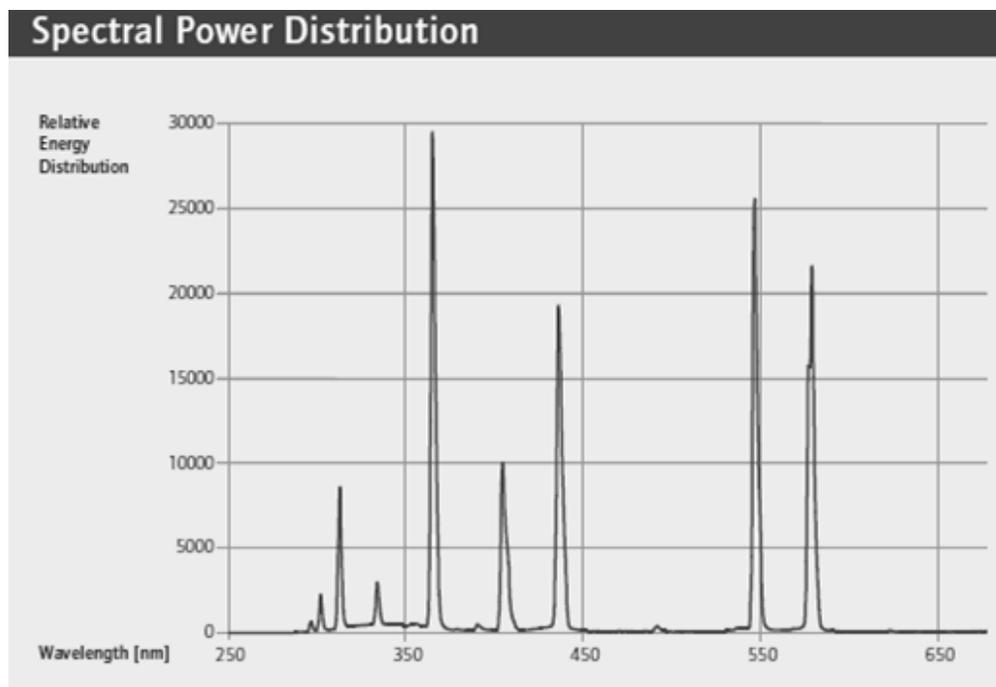


Figure 2-3: The spectral power of the SEPAP 12/24. Peak maximums are found at 290, 313, 365, 405, 436, 547 and 579 nm. Reproduced from reference ³¹.

Initially, qualitative samples were used to determine general degradation times of the film without pesticides and with Pyrinex 480 and Round Up. Samples of treated and untreated film were then placed in the SEPAP for quantitative analysis (table 2-4). The films were dosed with pesticide in a four-walled apparatus. Both film sample and apparatus were weighed prior to and after dosing to accurately calculate the amount of pesticide that came into contact with the film. After dosing, samples were allowed to dry for three days. Samples were then placed into SEPAP holders and exposed to radiation in the SEPAP device. Samples were periodically analyzed using FTIR in transmission mode. All tests were exposed until fragmentation occurred, in a single blind fashion.

Table 2-4: Samples exposed in the SEPAP device.

Film with no pesticide
Film with 0.0035 g \pm 0.0005 g of Pyrinex 480 per m ² of film
Film with 0.0062 g \pm 0.0005 g of Pyrinex 480 per m ² of film
Film with 0.0261 g \pm 0.0005 g of Round Up per m ² of film
Film with 0.0379 g \pm 0.0005 g of Round Up per m ² of film

2.4.3.3 Oven

Samples of film (both with and without pesticides) were then placed in a gravity oven at 60 and 80 °C (table 2-5). The films were dosed with pesticide in the same manner as above and again were allowed to dry for three days. Samples were placed into FTIR film holders and warmed in the oven. Samples were periodically analyzed using FTIR in transmission mode and positions of samples within the oven were rotated. All samples were exposed until fragmentation occurred, in a single blind fashion.

Table 2-5: Samples exposed in the oven at a variety of temperatures.

Temperature	Description
60 °C	Film with no pesticide
	Film with 0.0080 g \pm 0.0005 g of Pyrinex 480 per m ² of film
	Film with 0.0106 g \pm 0.0005 g of Pyrinex 480 per m ² of film
	Film with 0.0207 g \pm 0.0005 g of Round Up per m ² of film
	Film with 0.0295 g \pm 0.0005 g of Round Up per m ² of film
70 °C	Film with no pesticide
	Film with 0.0044 g \pm 0.0005 g of Pyrinex 480 per m ² of film
	Film with 0.0096 g \pm 0.0005 g of Pyrinex 480 per m ² of film
	Film with 0.0192 g \pm 0.0005 g of Round Up per m ² of film
	Film with 0.0452 g \pm 0.0005 g of Round Up per m ² of film
80 °C	Film with no pesticide
	Film with 0.0035 g \pm 0.0005 g of Pyrinex 480 per m ² of film
	Film with 0.0062 g \pm 0.0005 g of Pyrinex 480 per m ² of film
	Film with 0.0261 g \pm 0.0005 g of Round Up per m ² of film
	Film with 0.0379 g \pm 0.0005 g of Round up per m ² of film

2.5 Determining the Stabilizer Capacity of Pesticides

As previously discussed, there are five categories of stabilizer mechanisms. Briefly, a) UV screeners block UV light decreasing the energy that the polymer is exposed to, b) chain breaking donor and c) acceptor stabilizers prevent free radical propagation, d) peroxide decomposers break down species that cause propagation, and e) metal deactivators complex metals decreasing propagation sites. Of these only chain breaking donors/acceptors and UV screeners affect the PE prior to oxidation (scheme 1-2). Therefore, only these three methods of stabilizing were considered as potential causes of the delayed degradation.

2.5.1 UV Screeners

If a pesticide has UV screener capacity, it would show a delay in degradation in the field and photo-accelerated exposure environment, but not in the thermal-accelerated environment. To confirm suspected UV screener capacity, the UV absorbance of the pesticide should also be analyzed.

2.5.1.1 Theory

The UV absorbance of a chemical can predict if it can act as a UV screener²⁴. However, the ability to absorb UV does not necessarily indicate that a chemical *is* a screener because the species may not be dissipating UV energy²⁴. Therefore the UV absorbance should be compared with degradation in a photo environment to classify the effect the absorption is having.

2.5.1.2 Method

The UV-vis absorption spectra of pesticide-treated films were compared with the absorption spectra of untreated films without pesticides to determine whether there was noticeable additional absorption in the UVA and UVB parts of the spectrum.

2.5.2 *Chain Breaking Donors*

If a pesticide had donor capacity it would show a delay in PE degradation in all of the exposure environments, although the strength of the effect may differ in the different environments depending on the donor capacity. The delay in PE degradation is a result of the chain breaking donors being able to donate atoms or electrons to different free radicals, preventing further propagation (section 1.4.1.2).

2.5.2.1 Laboratory Study

2.5.2.1.1 Theory

Measuring the redox potential of a pesticide can suggest whether or not the pesticide has the capacity to act as a chain breaking donor. As chain breaking donors are important materials in the study of food there are a variety of tests one can use to determine oxidation or reduction of a chemical species³². Most of these methods work through tracking the colour change that follows the occurrence of a redox reaction.

The formation of a phosphomolybdenum complex is one method to test chain breaking donor capacity, specifically designed to determine if there is a reducing agent present in the solution which causes the reduction of Mo (VI) to Mo (V)³³. The oxidation state (VI) of molybdenum is uncoloured when in the form of phosphomolybdenum, but, when reduced to the oxidation state (V), the solution turns green. Therefore, if a chemical is added to phosphomolybdenum and a green colour is formed, the chemical is a reducing agent that can act as a chain breaking donor.

2.5.2.1.2 Method

0.1 mL of Round Up and 0.1 mL of Pyrinex 480 was mixed with 1 mL of reagent (0.6 M sulphuric acid, 28 mM sodium phosphate, 4 mM ammonium molybdate) and incubated in a

water bath for 90 min at 95 °C. The samples were allowed to cool and the absorbance at 695 nm was measured using a Genesys 10 UV visible spectrometer. Samples were referenced against a blank that was treated identically but lacked pesticide. Caffeine, a known hydroxyl radical scavenger³⁴, was used as a positive control and citric acid was used as a negative control as it is known to prevent oxidation from occurring³⁵. All samples were measured at a concentration of 0.05 g/L.

2.5.2.2 Theoretical Calculations

2.5.2.2.1 Theory

The primary antioxidant capacity of a pesticide can be estimated theoretically by computing the Bond Dissociation Energy (BDE) required to dissociate a hydrogen atom. This calculation determines the different energies of the neutral molecule and the dissociation products (Equation 2-1)³⁶,

$$\text{BDE (RH)} = E_{\text{RH}} - E_{(\text{R}^* + \text{H}^*)} \quad (2-1),$$

where E_{RH} indicates the energy of the neutral molecule and $E_{(\text{R}^* + \text{H}^*)}$ indicates the energy of the radical product.

Lower BDE indicates that the molecule is more likely to donate a hydrogen atom and thus act as a chain breaking donor³⁷. DiLabio et al. studied a variety of different mechanisms to determine BDE of a hydrogen atom, listing which methods were more appropriate³⁷. Leopoldini et al. reviewed the research that has been done on polyphenolic compounds using theoretical and computational methods³⁶. Their paper clearly described the literature results on hydrogen atom transfer, electron transfer and metal chelation in relation to polyphenols and concluded that most polyphenols appear to scavenge free radicals through hydrogen atom transfer³⁶. Mazzone et al. demonstrated that antioxidant energies determined experimentally could be replicated to some

extent using computational chemistry and the results from the computational studies were seen to allow rationalization and confirmation of the experimental data³⁸. Wright et al. determined a method of correction for each calculation determining the BDE of X-H where different corrections were applied depending on X, where X was a heavy atom from helium to argon.³⁹ As the above methods were used to calculate the BDE of different stabilizers, and pesticides may act as stabilizers, the calculations may be applied to pesticides as long as the same restraints are followed.

Another method of determining stabilizer capacity is to determine how likely a molecule is to donate an electron. Gázquez et al. developed a concept of calculating the electrodonating and electroaccepting powers of different molecules⁴⁰. The calculation is based on a previously used charge transfer model from the second order Taylor series expansion of the energy as a function of the number of electrons⁴⁰. The energy change in this equation is related to the chemical potential and hardness, which is associated with electron saturation in an electrophilic species⁴⁰. The combination of these different ideas was followed by an implication of the calculation for electrophilicity being approximated through the ionization potential and electron affinity as shown in the following equation for electrodonating power ω^- (Equation 2-2)⁴⁰,

$$\omega^- = (3I+A)^2 / 16 (I - A) \quad (2-2),$$

where I is the ionization potential and A is the electron affinity⁴⁰.

The ionization potential is calculated as the energy difference between the positively charged and neutral molecule. Electron affinity is calculated as the energy difference between the neutral and negatively charged molecule. Calculating the energy difference can be done vertically by using the same optimized structure of the neutral molecule and ion, or adiabatically

by using the optimized structure for the neutral molecule and the optimized structure for the ion⁴¹.

Previously published research led to the creation a reference for comparing electrodonating power⁴²⁻⁴⁴. The electrodonating power of sodium was calculated because it is known to be very likely to donate an electron and then this value was used as a reference for comparison with all other molecules⁴²⁻⁴⁴. The electrodonating index (Equation 2-3),

$$Rd = \omega^-_{\text{substance}} / \omega^-_{\text{Na}} \quad (2-3),$$

where Rd is the electrodonating index, $\omega^-_{\text{substance}}$ is the electrodonating capacity of the molecule being studied and ω^-_{Na} is the electrodonating capacity of sodium, can then be used to calculate how likely the molecule is to act as a chain breaking donor by donating an electron⁴⁵. If the Rd value is one, the molecule is as likely as sodium to donate an electron. If it is less than one, the molecule is more likely to donate an electron than sodium.

As theoretical calculations are often performed in the gas phase, thus ignoring interactions with other molecules, it may be important to consider differences occurring in energy when a solvent is added⁴¹. Any solvent can stabilize charge separation in the molecule, especially polar solvents which can change the energy, electron density and associated properties of the molecules under study⁴¹. Considering a polar and nonpolar solvent, such as water and benzene, is therefore essential for determining how the molecular energies may change.

2.5.2.2.2 Method

All calculations were based on previous methods designed to measure antioxidant capacity and were performed with the Gaussian 09 code⁴⁶. The principal conceptual tool used was Density Functional Theory (DFT). DFT models the electron correlation by a function of electron density presenting an independent-particle model⁴⁷. This theory is constructed from

three different considerations: the integral of the density defines the number of electrons; the cusps of the density defines the position of the nuclei; and the heights of the cusps define the corresponding nuclear charges⁴⁷.

BDE was computed for every hydrogen atom bonded with a carbon, oxygen or nitrogen (unless atoms were equivalent) following the method described by Leopoldini et al.³⁶. DFT methods were used as they were previously shown to have high accuracy through benchmark tests when paired with Becke 3 Lee Yang Par (B3LYP)^{48,49} along with the good prediction of X-H bond energies that have been produced through this calculation³⁶. Each pesticide was optimized and the frequency computed without constraints at the B3LYP level using the 6-311⁺⁺G(d,p)⁵⁰⁻⁵² basis set⁵¹. The core orbitals in this basis set are a contraction of six primitive Gaussian Type Orbitals and the valence was split into three functions that are represented by three, one, and one primitive Gaussian Type Orbitals⁴⁷. The basis set also contains one set of diffuse s- and p- functions on heavy atoms, and a diffuse s-function added to hydrogen⁴⁷. Finally, the basis set has a single d- and p- type of polarization on heavy atoms⁴⁷.

All calculations were optimized to a minimum and corrected using zero point energy. Hydrogen atom energy was set to -0.500 hartree as a precaution against the lower energy that is received for a lone hydrogen atom calculation³⁶.

The electrodonating capacity of both pesticides was calculated using sodium as a reference. When calculating ionization potential and electron affinity, vertical calculations were used. Electrodonating calculations were run in the gas phase along with water and benzene as solvents using the Polar Continuum Model.

2.5.3 Chain Breaking Acceptors

If a pesticide had chain breaking acceptor capacity, it would cause a delay in degradation in all of the exposure environments, although the strength of the effect may differ in the different environments depending on the acceptor capacity. Since this is the same effect that will be seen for a chain breaking donor, it is not possible to determine the type of chain breaking reactions that may be occurring based solely on exposure environments.

2.5.3.1 Theoretical Calculations

2.5.3.1.1 Theory

Electroaccepting capacity can also be predicted using theoretical calculations. Gázquez et al.'s theory can be used to calculate the electroaccepting power, ω^+ , using equation 2-4⁴⁰,

$$\omega^+ = (I+3A)^2 / 16 (I - A), \quad (2-4)$$

where I is the ionization potential and A is the electron affinity.

Previous research has led to the creation of a reference for comparing electroaccepting power. The electroaccepting power of fluorine is calculated because it is known to be very likely to accept an electron and the value is used as a reference for comparison with all other molecules⁴²⁻⁴⁴. The electroaccepting index is calculated following equation 2-5,

$$Ra = \omega^+_{\text{substance}} / \omega^+_{\text{F}} \quad (2-3),$$

where Rd is the electroaccepting index, $\omega^+_{\text{substance}}$ is the electroaccepting capacity of the molecule being studied and ω^+_{Na} is the electroaccepting power of fluorine. If Ra is equal to or greater than one, the molecule is as good or a better electron acceptor than fluorine⁴⁵. Therefore this calculation suggests whether a molecule will be able to act as a chain breaking acceptor.

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Chapter 3. Results and Discussion

3.1 Degradation Measurements

Measuring three different samples of film with different exposure times in the SEPAP to determine the most descriptive peaks for oxodegradation in this study resulted in the expectations laid out in section 2.3.1 (table 3-1). A representative spectrum showing these peaks is found in figure 3-1. Merged peaks were deconvoluted to determine peak position and area.

Table 3-1: Results for peaks analyzed for PE degradation using FTIR.

Peak cm^{-1}	Functional Group	Observations After Graphing the Peak Change over Time
1785	C=O stretch cyclic esters ^{1,2}	Peak merged with 1740 cm^{-1} and 1715 cm^{-1} peaks, peaks overall had large change in absorbance units as exposure time increased
1740	C=O stretch acyclic esters ¹	Peak merged with 1785 cm^{-1} and 1715 cm^{-1} peaks, peaks overall had large change in absorbance units as exposure time increased
1730	C=O stretch aldehyde ³	No peak
1715-1720	C=O stretch ketone, carboxylic acid ^{1,3,4}	No peak found at 1720 cm^{-1} Peak at 1715 cm^{-1} was merged with 1785 cm^{-1} and 1740 cm^{-1} peaks, peaks overall had large change in absorbance units as exposure time increased
1185	C-O stretch, carboxylic acid ^{1,4}	Peak at 1185 cm^{-1} showed small increase in peak area and height absorbance as exposure time increased
1640	C=C stretch ⁵	Small increase in peak area and height absorbance as exposure time increased
1463	C-H scissoring bend ⁶	Used as reference peak
915	=C-H bend ⁵ O-H bend ⁷	Small increase in peak area and height absorbance as exposure time increased

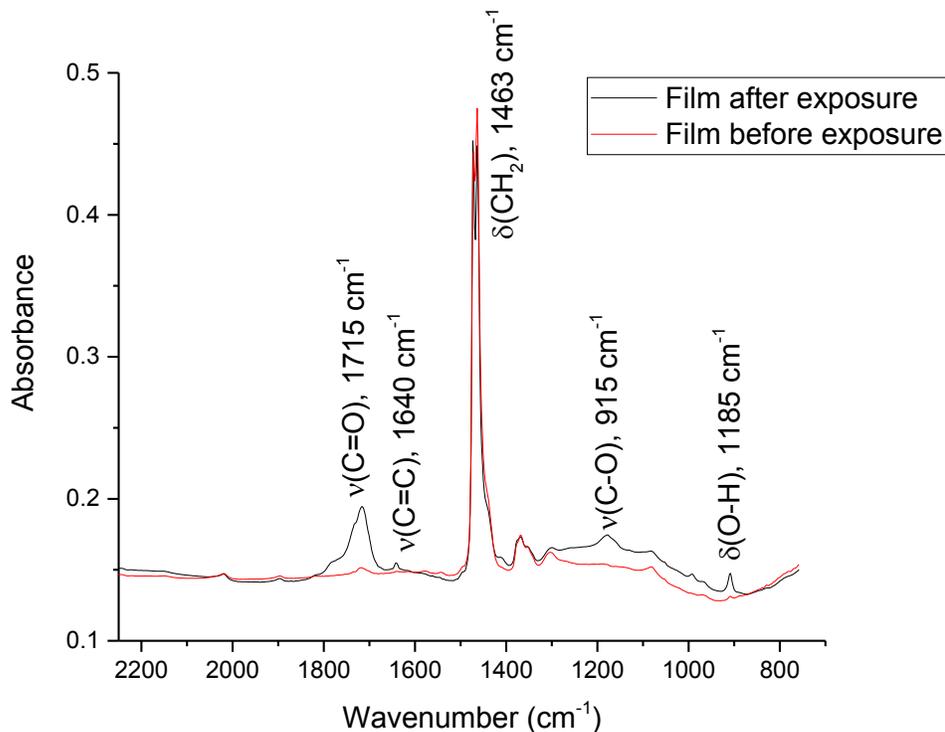


Figure 3-1: IR absorbance in transmission mode of a PE film prior to and after 35 hours in the SEPAP device. The same piece of film was measured.

Similar to other FTIR analyses on oxodegradable PE⁸⁻¹⁶, the peaks in the 1715 cm⁻¹ region had the largest increase in absorbance as exposure time increased. This was expected because when PE degrades oxygen content increases and C=O stretching vibrations have characteristic frequencies in this range.

Though previous reports cite peaks associated with degradation at both 1715 cm⁻¹ and 1720 cm⁻¹, within this study there was not an obvious peak at 1720 cm⁻¹. Both of these peaks are associated with the stretching of C=O found in carboxylic acids and ketones. These functional groups should be present as degradation proceeds, as they are products of carbon groups reacting with oxygen. (For more details refer to Appendix I). The small peak found at 1185 cm⁻¹ in figure 3-1 corresponds to the C-O stretch of carboxylic acid⁴, indicating that

carboxylic acid is likely present. However, the much larger peak at 1715 cm^{-1} would suggest that there is more than just carboxylic acid contributing to this peak. Thus, it can be assumed that as degradation proceeded both carboxylic acids and ketones were present.

To measure the degradation, many studies measure the carbonyl index (section 2.3.1)^{12,13,16–26}. To be consistent with literature studies of PE degradation, the carbonyl index was considered one method of quantifying the degradation. However, we hypothesized that this method does not account for the different peak developments within the 1715 cm^{-1} envelope (figure 3-2). Being able to quantify each peak would allow better analysis of what is occurring during degradation.

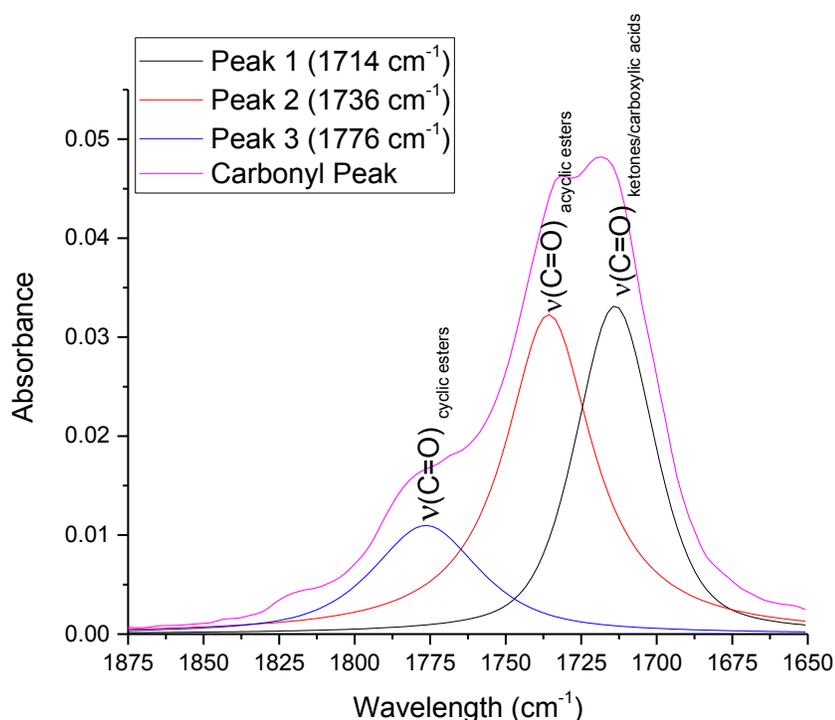


Figure 3-2: A portion of an absorbance spectrum measured for a film (without pesticide application) after 35 hours spent in the SEPAP device. The region between 1650 and 1875 cm^{-1} is shown to highlight the multiple peaks in the 1715 cm^{-1} region, $R^2=0.999501$.

To account for the multiple peaks at 1715 cm^{-1} , the total area of the peaks and the deconvoluted areas were measured. The deconvoluted areas allowed measurements of three peaks with maxima at 1714 , 1736 , and 1776 cm^{-1} , determined by self-deconvolution finding the maximum of peaks referenced within the literature¹⁻⁴. Both the measurements of the total and deconvoluted area had large associated error and no visible trend with degradation. The lack of trend is likely due the multiple mechanisms by which degradation can occur in PE (Appendix I). The multiple reactions cause different functional groups to occur during degradation and although the degradation amount is comparable, the functional groups may not be. As a result, only measurements of carbonyl index were used for analysis of degradation as seen in later sections.

3.2 Pesticides and Plastic Mulch Films

Pesticide was not observed running off plastic mulch after application and were clearly visible on all films after application, as shown in figure 3-3. The persistent presence of pesticide on plastic mulch film has also been reported previously in the literature²⁷.



Figure 3-3: Photos showing mulch films. The film on the left did not have pesticide applied. The film on the right had Round Up applied.

To confirm that FTIR was suitable for analyzing films with pesticide applications, the ATR spectra of concentrated pesticide were measured. An assumption was made that if the pesticide did not absorb in the carbonyl index regions, which would be used to analyze the degradation of PE, then measuring degradation with FTIR would not be problematic. An ATR absorbance spectra of Pyrinex 480 is shown in figure 3-4 and Round Up in figure 3-5, both of which demonstrate that the pesticides do not absorb in the 1715 and 1463 cm^{-1} region.

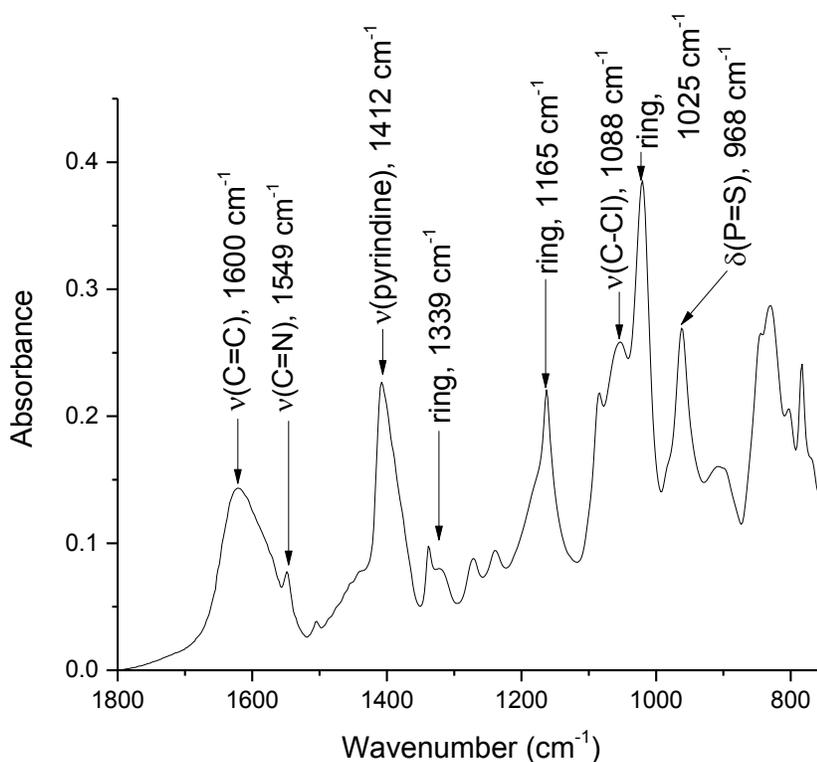


Figure 3-4: ATR absorbance spectrum of Pyrinex 480.

Areas where Pyrinex 480 did absorb represent the key features of chlorpyrifos: C=C stretching in the ring in the region of 1600 cm^{-1} ⁷; C=N stretching at 1549 cm^{-1} ²⁸; aromatic ring vibrations at 1412, 1339, 1165, and 1025 cm^{-1} ²⁸; Cl-C stretching at 1088 cm^{-1} ²⁸; P=S stretching at 968 cm^{-1} ²⁸. Carbon-hydrogen stretching was not included in this study.

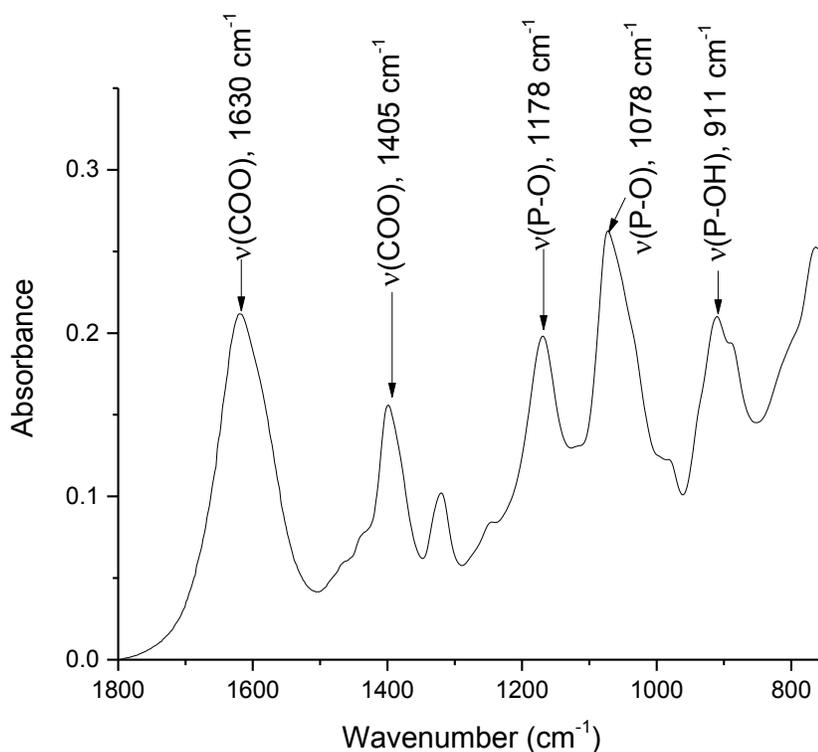


Figure 3-5: ATR absorbance spectrum of Round Up.

Areas where Round Up did absorb represent the key features of glyphosate: carboxylic acid stretching at 1630 and 1405 cm^{-1} ²⁹; vibrations from the phosphonate groups at 1178, 1078 and 911 cm^{-1} ²⁹. Due to the carboxylic acid group on glyphosate (figure 1-4) it was expected that the scan would show a peak at 1715 cm^{-1} , but as seen in this spectrum, the regions of 1715 and 1463 cm^{-1} are not affected by the addition of Round Up. Although the lack of this peak is unexpected, the peak also was not present in a study analyzing FTIR spectrum of glyphosate²⁹ and is therefore unlikely to be problematic.

ATR measurements were used to determine if the pesticide migrated from the top of the film. Both the top and bottom of the film were analyzed and a comparison was made between the spectra of film prior to and after pesticide addition (figures 3-6 and 3-7).

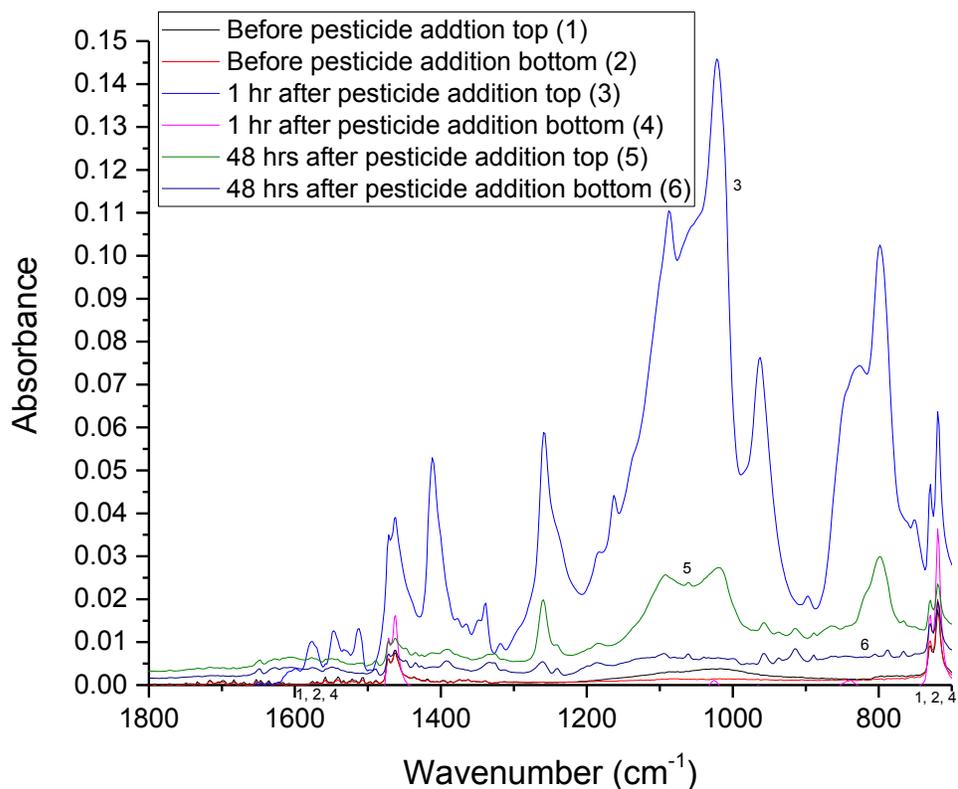


Figure 3-6: ATR spectra of PE film after addition of 0.0066 ± 0.0005 g of Pyrinex 480 per m^2 of film without degradation exposure.

The IR spectrum for the top of the film after being sprayed with Pyrinex 480 compared to pre-addition of pesticide is very similar to what was measured in the spectra of Pyrinex 480, as expected. Within the two days the loss of peak height likely indicates that some aspect of Pyrinex 480, if not the whole thing, is dissipating into the air. Since Pyrinex 480 has volatile components, the decrease in absorbance is likely from the loss of the volatile aspects. Samples measured after more than two days did not show significant differences and therefore are not represented on figure 3-6. The lack of difference in ATR scans after two days indicates that Pyrinex 480 is remaining on the film and therefore, even though within the first 48 hours a large

amount of the pesticide is likely dissipating, the presence of pesticide on either surface of the film is still significant.

Comparing the top of the film after pesticide application to the bottom of the film after application indicates that Pyrinex 480 is likely not migrating through the film. This is known because there is very little difference between the bottom of the film pre-pesticide application, after one hour and after two days. When determining how Pyrinex 480 affects degradation, this result correspond with data that was observed after degradation analysis and is discussed further in section 3.3.1.

Figure 3-7 shows the ATR spectrum of PE film after application of Round Up.

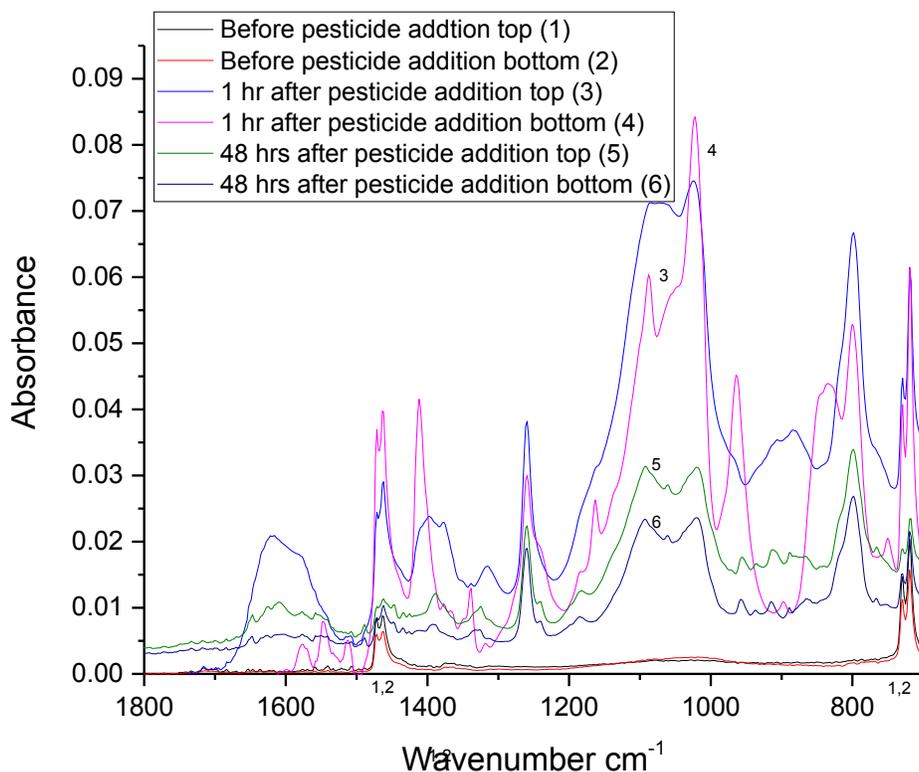


Figure 3-7: ATR spectrum of PE film after addition of 0.0261 ± 0.0005 g of Round Up per m² of film without degradation exposure.

A comparison between the top and the bottom of the film showed that Round Up is migrating immediately through the film. Between one hour and 48 hours the amount of pesticide on the film was decreased. This observation was determined from the decrease in peak amplitude between the measurements at one and 48 hours. After 48 hours the spectra overlapped and for clarity, they are omitted from figure 3-7. Again, although a decrease was seen within the 48 hours the lack of change after 48 hours indicates the amount of Round Up remaining on the film is significant. Though ATR measurements indicate that Round Up appears to be migrating through the film, there was no evidence of swelling in the film as observed by eye. As all the measurements described here are sensitive to changes on a length scale that is small compared to changes in polymer conformation, any major changes to the film associated with the migration of Round Up (or some of its constituents) would not be likely to interfere with the interpretation of these results.

Following previous literature³⁰ on mulch films and pesticides, the films were scanned prior to pesticide application using UV-vis spectrometry and after pesticide application at one hour, two days, two weeks and one month. As PE does not naturally contain any conjugated bonds that can absorb energy in the UV region, a UV spectrum of PE should be flat. Adding pesticides with conjugated bonds, such as those found within Pyrinex 480 and Round Up, will cause absorption peaks. Thus it is possible to determine the presence of pesticide in or on the film. The change in UV absorbance over time for a film sprayed with Pyrinex 480 and Round Up is shown in Figure 3-8 and Figure 3-9 respectively.

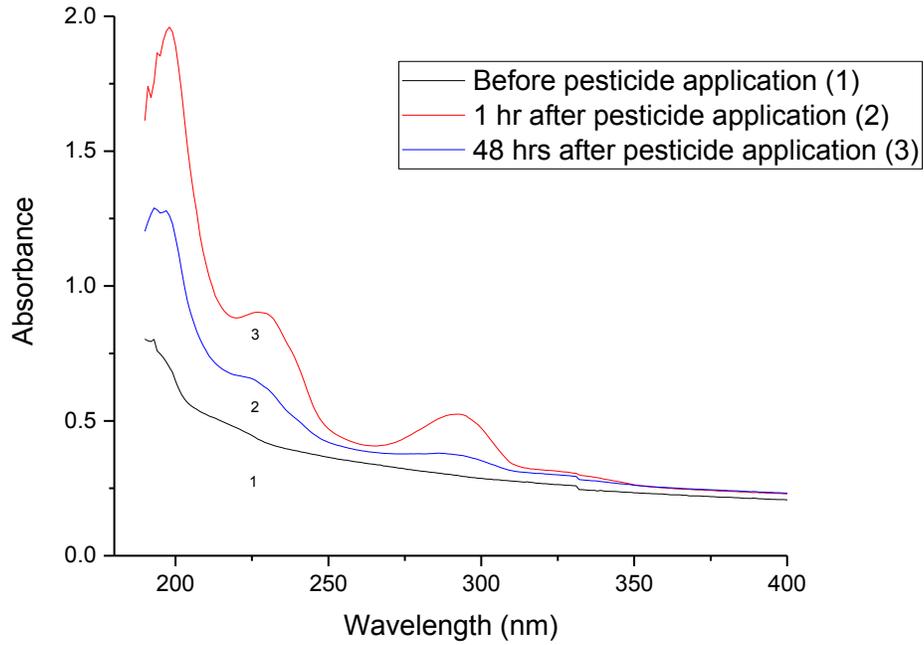


Figure 3-8: UV absorbance of PE film after application of 0.0066 ± 0.0005 g of Pyrinex 480 per m^2 of film.

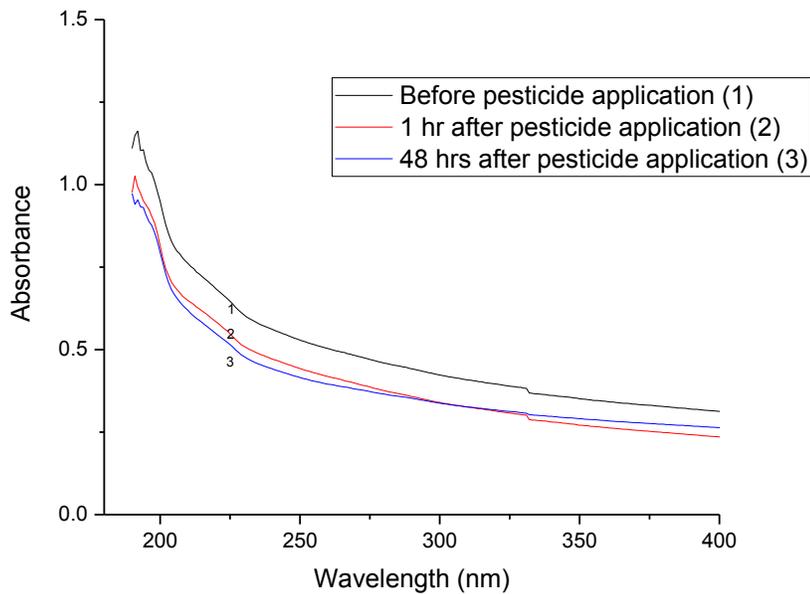


Figure 3-9: UV absorbance of PE film after application of 0.0261 ± 0.0005 g of Round Up per m^2 of film.

Figure 3-8 indicates that the Pyrinex 480 is present on the film in higher concentrations at one hour than in two days. UV spectra collected after more than two days did not show noticeable changes from the two day spectra and therefore are not represented within figure 3-8. The lack of change after two days agrees with measurements completed using ATR.

Figure 3-9 does not show any changes in the spectrum after the addition of Round Up to the PE. As ATR results for the same films indicated that Round Up was present on the plastic (figure 5-6) the amount of Round Up on the film was below the detection limit for the UV-vis spectrometer used.

3.2.1 Exposure Environments

In order to determine the possible effects of the pesticides when applied to the films, a field test was used along with accelerated photo and thermal environments in a SEPAP 12/24 device and a gravimetric oven.

3.2.1.1 Field

Field studies are an essential part for any test on degradable agriculture mulch films because they are the only environment where realistic conditions for degradation are met. The realistic conditions include a variety of factors that do not differ in controlled laboratory degradation environments and, therefore, the results obtained in the field were expected to have a large amount of associated variation^{10,31-33}. Within the field, the only samples that were seen to have traceable degradation were the untreated samples (figure 3-10). Apart from the untreated samples the change in degradation values over time for samples with applications of pesticide was minimal. We hypothesize that this was the result of pesticide application to the films, as pesticides were seen to cause degradation delays in accelerated environments (sections 3.3.1.2,

3.3.1.3). This implies that agriculture use of oxobiodegradable mulch films and pesticides together will drastically change the expected degradation time of the films.

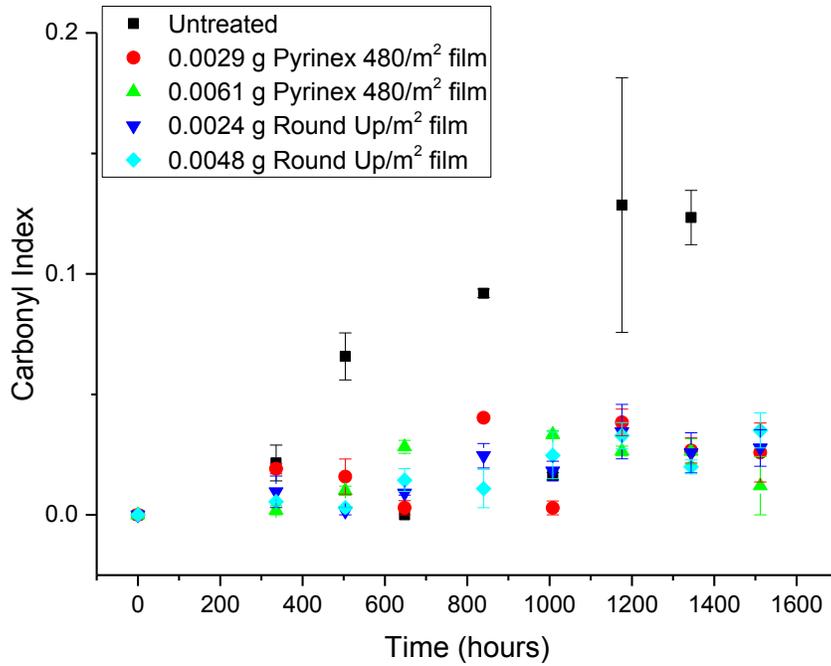


Figure 3-10: The difference in carbonyl index versus exposure time in the field. Error bars represent the standard deviation between two different samples. Each sample was a unique piece of film as samples could not be replaced in the field.

It should be noted that the unexposed samples did not degrade until eight weeks and the test was only run for nine weeks (due to the end of the season). Therefore, it is possible that extending the length of the field test by a few weeks would have resulted in degradation of the samples with applied pesticides. It was noted that when the remaining films were removed at the end of the season all films had physical characteristics similar to PE when degradation is beginning to occur (e.g. they were easily torn). However, this observation was not consistent with the associated carbonyl index measurements.

3.2.1.2 SEPAP

Within the SEPAP, the differences between the effects of pesticide type or pesticide dose were more pronounced than within the field. This was expected as the SEPAP is a photo accelerated environment that has controlled photo and thermal exposure. An hour in the SEPAP is estimated to be approximately 1.2 days in a European climate³⁴. The European climate is considered temperate, whereas the Canadian climate is often referred to as cold. Therefore, an hour in the SEPAP will be much longer than 1.2 days in a Canadian climate. Figure 3-11 shows the carbonyl index for untreated films and films sprayed with two different concentrations of Round Up and Pyrinex 480 after exposure in the SEPAP.

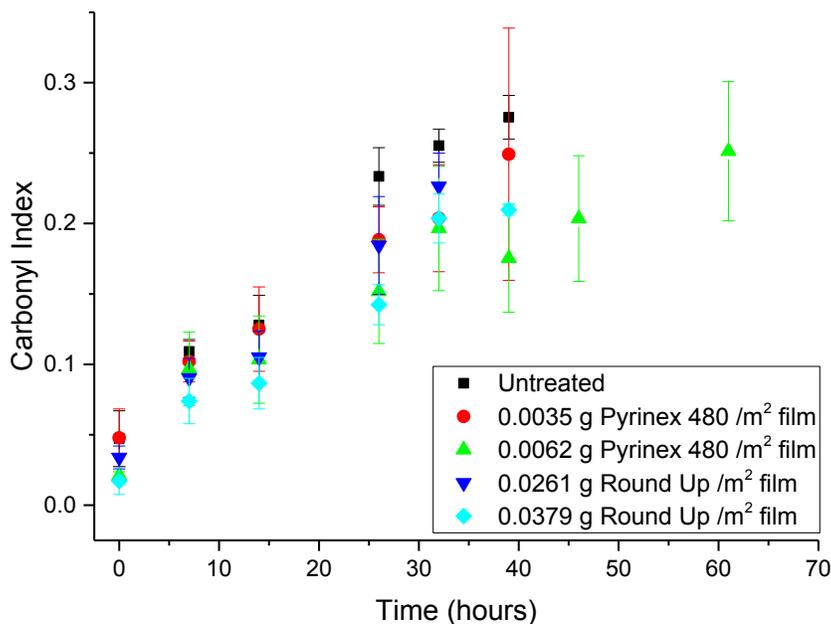


Figure 3-11: The change in carbonyl index over hours of exposure in the SEPAP for samples with and without applied pesticide. The error bars indicate the standard deviation between a minimum of two samples.

Samples treated with 0.0261 g/m² of Round Up fragmented the quickest (32 hrs) but did not have the highest carbonyl indexes. Instead, the untreated samples had the highest carbonyl index. Pyrinex 480 with 0.0062 g/m² was the sample that fragmented the slowest (61hrs), and also had the lowest carbonyl index. This indicates that the carbonyl content was delayed along with the degradation. The other two samples exposed to pesticide and the untreated samples had similar carbonyl indices (although the untreated sample was on average the highest) and all degraded at the same time (39hrs).

As PE degrades by incorporating oxygen into the chain, it is expected that the amount of carbonyl groups should increase. Therefore, degradation of 0.0261 g/ m² of Round Up seems to fail the assumed mechanism of degradation because these samples fragmented the quickest but did not have the lowest carbonyl index. This is likely from incomplete coverage of Round Up on

the film. As this study attempted to replicate pesticide applications that would occur in agriculture settings, the pesticide was simply sprayed onto the films as opposed to the films being soaked in pesticide or painted with pesticide. As a result, the pesticides were not applied evenly and the calculated concentration refers to the average sample.

The data from the SEPAP study indicate that films with applications of Pyrinex 480 are likely to have delayed degradation compared to untreated films in a photo-oxidative environment and films with applied Round Up are likely to have the same or quicker degradation as untreated samples. As expected in both applications of pesticide, the higher treatment of pesticide had lower carbonyl indices than the lower treatment, indicating higher amounts of pesticide have a more pronounced effect on degradation.

Untreated samples and samples with the longest delay in degradation in the SEPAP had a difference in 22 hours of degradation time (starting at 39 hours and ending at 61 hours). Even if the Canadian and European climates are assumed to be the same this difference in SEPAP exposure time would be equal to five weeks in the field (starting at 6.7 weeks, ending at 10.5 weeks). Field samples were only measured until nine weeks due to the end of the season suggesting that the lack of degradation in the field is likely from the short time frame of exposure for field samples. The field data indicates that applying pesticides to the degradable films delays degradation and therefore the pesticides likely act as a stabilizer. Overall, the SEPAP data exhibited the same result. However, the difference between the effects of the two pesticides in the SEPAP suggest that Pyrinex 480 is a stronger stabilizer in the photo-oxidative environment than Round Up.

3.2.1.3 Oven

Figure 3-12, 3-13 and 3-14 show the change in carbonyl index as a function of time for oven temperatures of 60, 70 and 80° C, respectively. At all temperatures, sample degradation was more clearly defined than within the field and followed more obvious trends than in the SEPAP.

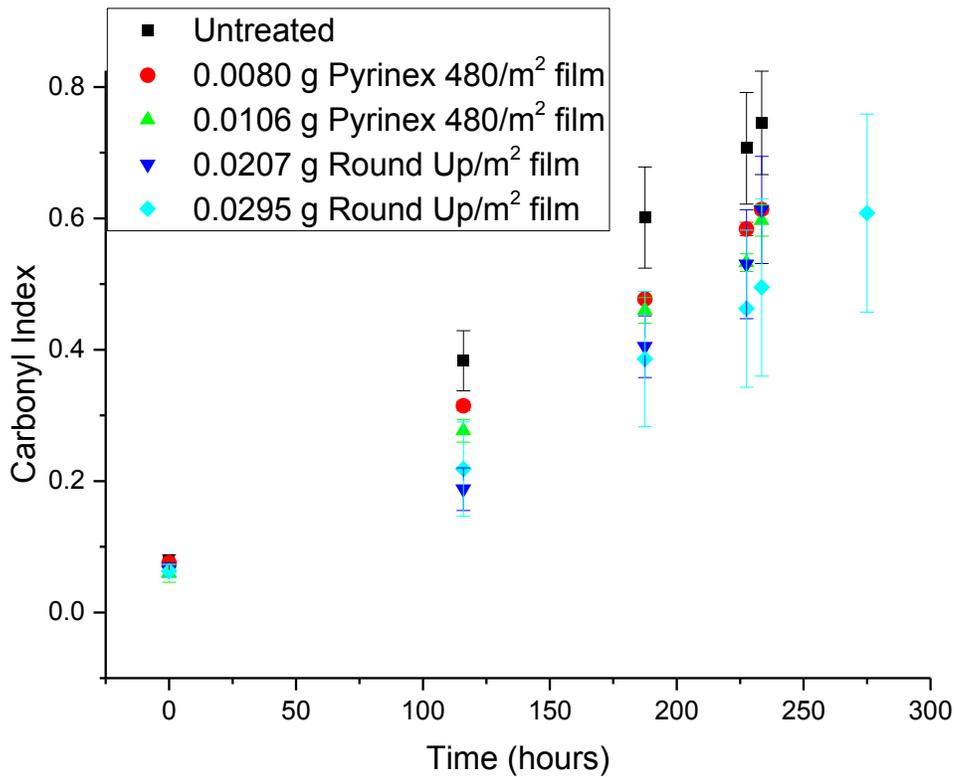


Figure 3-12: The carbonyl index as a function of exposure time in the oven at 60 °C for samples with and without applied pesticide. Error bars represent the standard deviation between a minimum of two samples.

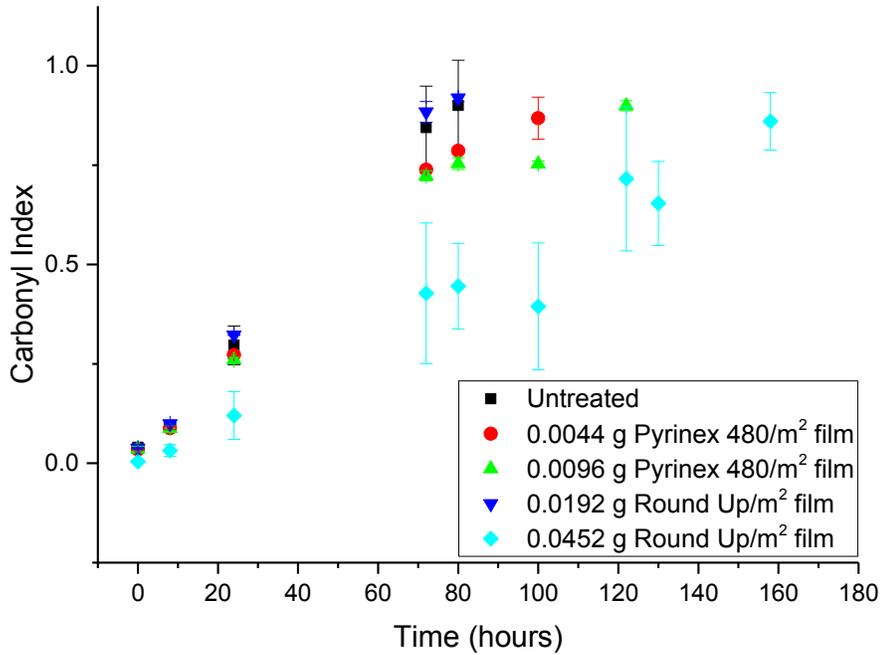


Figure 3-13: The carbonyl index over hours of exposure in the oven at 70 °C for samples with and without applied pesticide. Error bars represent the standard deviation between a minimum of two samples.

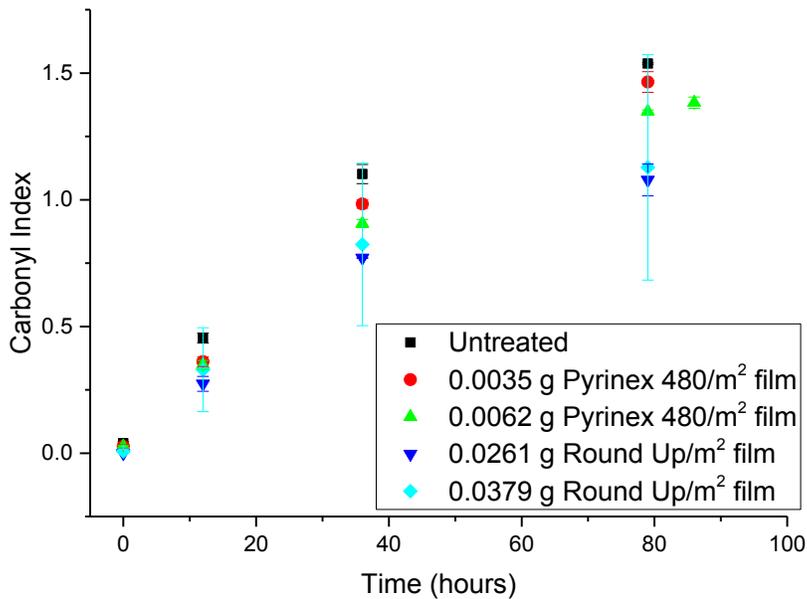


Figure 3-14: The carbonyl index as a function of exposure time in the oven at 80 °C for samples with and without applied pesticide. Error bars represent the standard deviation between a minimum of two samples.

In the oven at 70 °C the untreated samples consistently had higher carbonyl indices than all of the other samples, except for the Round Up application with 0.0192 g/m². At 60 and 80 °C the untreated sample consistently had the highest carbonyl index. The high carbonyl indices for untreated samples at all temperatures indicate that both pesticides delay degradation in a thermal environment and confirm previous observations that both pesticides have stabilizer effects. The high carbonyl indices for the application of 0.0192 g/m² of Round Up in the oven at 70 °C is likely a result of non-uniform pesticide application since this was not observed at the other two temperatures.

Samples with the higher dosage of Round Up had the lowest carbonyl indices for all temperatures and were the slowest to fragment except at 80 °C. At 80 °C samples with applications of 0.0062 g/m² of Pyrinex 480 fragmented the slowest. The slower fragmentation of the Pyrinex 480 sample at 80°C was unexpected as both samples that were exposed to Round Up have lower carbonyl indices. This may be a result of instability of the pesticides due to the higher temperature in the oven.

3.2.2 *Summary of Different Exposure Environments*

The carbonyl index for each of the different oven temperatures had an overall standard deviation that was much lower than the SEPAP, despite the higher values of carbonyl index. This is likely influenced by the lower amounts of radiation that occurs in the oven. In the oven only thermal energy is impacting the samples. The smaller carbonyl indices determined within the SEPAP and field are likely a result of both ketones and hydroperoxides being decomposed, as opposed to just hydroperoxides in the thermal environment³¹. The 60 and 70 °C oven tests would suggest that, in a thermal oxidative environment, Round Up application delays the degradation of

the film for longer than Pyrinex 480. This suggests that Round Up has more thermal stabilizer capacity than Pyrinex 480.

Within the field, SEPAP and oven environment, the carbonyl index values for the untreated samples were the highest, despite the untreated samples not always degrading the quickest. This indicates that the untreated samples always had the most oxygen incorporated into their backbones.

Results from the field differed qualitatively from those obtained in accelerated test environments. Films in the field had Round Up levels ten times less than in the accelerated testing (a result of the applicator used in the accelerated testing, though both dosages used in the laboratory and the field are within the range of recommended application rates for Round Up³⁵). Data obtained from the SEPAP and oven tests for Round Up suggests that the difference between untreated samples in the field and the samples with Round Up applied should be much less than what was observed. Also carbonyl indices for both samples with applied Round Up and Pyrinex 480 should be closer to carbonyl indices for untreated samples in the field if the accelerated testing is representative of what is occurring in the field. Since this is not the case, there is likely a factor in the field, such as temperature fluctuations, that increase the effect the pesticides have on degradation. Further study is needed to define what is occurring in the field and not in the accelerated test environments, as this factor may influence the extent of pesticide application's impact on degradation.

The longer time to fragmentation observed in the SEPAP for samples with the higher concentration of Pyrinex 480 suggests that Pyrinex 480 can act as a UV screener. A large increase in time in a photo-accelerated environment, which is not always seen in a thermal environment suggests a reaction is occurring that is UV sensitive. Interestingly, when ATR

spectra was compared for the top versus the bottom of the film with applied Pyrinex 480 the pesticide was not seen to be migrating through the film (section 3.2). ATR spectra from films with applied Round Up however, did demonstrate pesticide migration. As photo-oxidative degradation is known to be more sensitive to the top of the film (section 1.3.1) the ATR results are consistent with the possibility that Pyrinex 480 may act as a UV screener and Round Up does not.

Table 3-2 summarizes the end points that occurred in the different studies. The reader is reminded that for all films, degradation points were taken as the measurement before the film could no longer be measured due to complete fragmentation.

Table 3-2: End point of film within the different studies. The error in CI corresponds to the standard deviation of two or more measurements for that given time.

Exposure	Pesticide Applied	Hours of Exposure	CI of Last Measurement
Field	No Pesticide	1344	0.123 \pm 0.010
	0.0029 g \pm 0.0005 g Pyrinex 480 per m ² of film	1512	0.025 \pm 0.010
	0.0061 g \pm 0.0005 g Pyrinex 480 per m ² of film	1512	0.012 \pm 0.010
	0.0024 g \pm 0.0005 g Round Up per m ² of film	1512	0.025 \pm 0.007
	0.0048 g \pm 0.0005 g Round up per m ² of film	1512	0.035 \pm 0.007
SEPAP	No Pesticide	39	0.275 \pm 0.020
	0.0035 g \pm 0.0003 g Pyrinex 480 per m ² of film	39	0.249 \pm 0.090
	0.0062 g \pm 0.0005 g Pyrinex 480 per m ² of film	61	0.251 \pm 0.050
	0.0261 g \pm 0.0005 g Round Up per m ² of film	32	0.226 \pm 0.020
	0.0379 g \pm 0.0005 g Round up per m ² of film	39	0.210 \pm 0.004
Oven at 60 °C	No Pesticide	233.5	0.597 \pm 0.020
	0.0080 g \pm 0.0005 g Pyrinex 480 per m ² of film	233.5	0.745 \pm 0.080
	0.0106 g \pm 0.0005 g Pyrinex 480 per m ² of film	233.5	0.614 \pm 0.006
	0.0207 g \pm 0.0005 g Round Up per m ² of film	233.5	0.613 \pm 0.080
	0.0295 g \pm 0.0005 g Round up per m ² of film	275	0.608 \pm 0.200
Oven at 70 °C	No Pesticide	80	0.900 \pm 0.100
	0.0044 g \pm 0.0005 g Pyrinex 480 per m ² of film	100	0.868 \pm 0.050
	0.0096 g \pm 0.0005 g Pyrinex 480 per m ² of film	122	0.900 \pm 0.010
	0.0192 g \pm 0.0005 g Round Up per m ² of film	80	0.919 \pm 0.009
	0.0452 g \pm 0.0005 g Round up per m ² of film	166	0.860 \pm 0.070
Oven at 80 °C	No Pesticide	79	1.538 \pm 0.004
	0.0035 g \pm 0.0005 g Pyrinex 480 per m ² of film	79	1.465 \pm 0.040
	0.0062 g \pm 0.0005 g Pyrinex 480 per m ² of film	86	1.383 \pm 0.020
	0.0261 g \pm 0.0005 g Round Up per m ² of film	79	1.078 \pm 0.060
	0.0379 g \pm 0.0005 g Round up per m ² of film	79	1.128 \pm 0.400

The lower carbonyl indices at the end point of degradation within the SEPAP are likely a result of increased radiation. In the SEPAP and field the films are exposed to both photo and thermal oxidation and it is possible that the PE backbone is broken down quicker and with less oxygen required³⁶. The possibility stems from photo radiation being strong enough to break carbon-carbon bonds (section 1.3.1).

Another possible explanation is that photo exposure can breakdown hydroperoxides and ketones, whereas thermal environments can only continue to breakdown hydroperoxides³¹.

Therefore in an environment lacking photo oxidation there will be a build-up of ketone groups within the molecule which will contribute to an increase in the carbonyl index.

3.3 Determining Stabilizer Capacity

The results from the tests carried out in the different exposure environments suggested that the pesticides were acting as stabilizers. The two pesticides studied in the laboratory had very different structures (section 2.1, figures 2-1 and 2-2). The different structures and differences in degradation delay in the different environments suggest that the pesticides are not acting through the same mechanism. As previously mentioned, Pyrinex 480 likely has UV screener capacity because of the long delay in a photo exposure environment. The shorter delay in the thermal exposure environments suggests Pyrinex 480 has a second method of delaying degradation. The degradation delay in the photo and thermal environment influenced by Round Up suggests that Round Up acts as a type of stabilizer, although it is unlikely that Round Up has UV screener capacity.

3.3.1 UV Screeners

3.3.1.1 Laboratory Study

UV screener capacity can be predicted from whether or not a chemical can absorb UV in the UVA and UVB region as these regions are associated with PE degradation.

The spectra of Pyrinex 480 indicates that it is a strong absorber in the UVB range (290-320 nm, figure 3-8). UVB is a strong contributor to the degradation of PE films and therefore this corresponds with the suggestion that Pyrinex 480 acts as a UV screener when applied to degradable PE film.

The UV spectra of Round Up dissolved in chloroform did not show peaks in the UVA or UVB region (figure 3-9). This corresponds with previous observations that it is unlikely Round Up has UV screener capacity.

3.3.2 *Chain Breaking Donors*

3.3.2.1 Laboratory Study

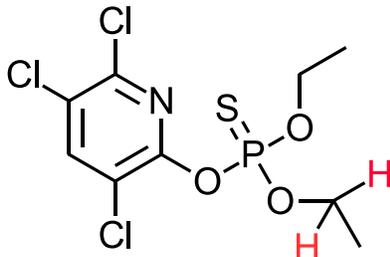
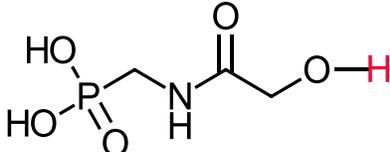
The chain breaking donor capacity measurement used in this study was based on a method used in food studies to determine stabilizer capacity³⁷. In this method the redox capacity of a chemical is measured by applying the chemical to a molecule containing molybdenum (VI). If the chemical has reducing capacity the molybdenum will become (V) and a colour change will occur (section 2.5.2). Caffeine was used as a positive control and citric acid as a negative control. In this test, both caffeine and Round Up were seen to act as reducing agents and therefore have chain breaking donor capacity. Pyrinex 480 and citric acid were not seen to act as reducing agents.

Environmental exposure test indicate that both Pyrinex 480 and Round Up can act as stabilizers separate from the UV screener capacity of Pyrinex 480 due to the delay in degradation in the thermal environment for both pesticides. This data indicates that Round Up may be delaying degradation through donating an atom or electron to break propagation chains in PE.

3.3.2.2 Theoretical Calculations

The bond dissociation energy (BDE) is known to represent how likely a molecule is to donate an atom³⁸. BDE was calculated for every unique hydrogen bonded to a carbon, oxygen, nitrogen or sulphur atom. Table 3-3 shows the lowest calculated BDE and the corresponding hydrogen atom(s).

Table 3-3 : The energy for the BDE of hydrogen in each pesticide computationally tested.

Pesticide	Lowest BDE for Hydrogen kJ/mol	Lowest hydrogen
Pyrinex 480 (chlorpyrifos)	397.2	
Glyphosate	302.1	

Polyphenol molecules that are expected to have strong stabilizer capacity have been calculated to have BDE of less than 350 kJ/mol³⁸. Therefore the BDE calculations indicate Round Up would be a good candidate for donating a hydrogen atom whereas Pyrinex 480 would not. This result is in agreement with the results obtained in the laboratory study. Interestingly, the BDE determined for Pyrinex 480 also corresponds with the UVB wavelength once again indicating that Pyrinex 480 can absorb UVB and likely act as a UVB screener.

The ionization potential and electron affinity of each atom was calculated using vertical calculations, computed in the gas phase and with benzene and water as solvents. These values were then used to obtain the electrodonating index (Rd) based on the equations by Gázquez et al.³⁹ and Martínez et al⁴⁰ (table 3-4).

Table 3-4: Electrodonating Index (Rd), under different solvent effects.

Pesticide	Solvent	Rd
Pyrinex 480 (chlorpyrifos)	None	1.39
	Water	1.84
	Benzene	1.56
Round Up (glyphosate)	None	1.34
	Water	1.30
	Benzene	1.32

When compared to sodium these results indicate that the active ingredient in both pesticides is less likely to donate an electron than sodium. However, the lower values obtained for Round Up in all solvent scenarios indicate that, between the two, Round Up is more likely to donate an electron than Pyrinex 480, which agrees with the BDE calculation and the laboratory study. The inconsistencies between the different solvent effects (i.e. for Pyrinex 480 the lowest Rd occurs with no solvent, and with Round Up it occurs with water) indicate that the Rd values for this study are dependent on what solvent is used in regards to the pesticide. More research is needed to define what the effects of solvents are for Rd calculations of pesticides.

All three tests regarding chain breaking donors were in agreement that Round Up has a higher capacity to donate electrons than Pyrinex 480. The capacity to donate an electron will help a species stabilize a free radical during chain propagation in either a photo or thermal oxidative environment. Therefore, the delay in degradation seen in Round Up for all three exposure environments corresponds with this data. The comparative longer delay that occurs in the thermal-oxidative environment likely indicates that the chain breaking donor effect is more stable without UV exposure. The different tests indicated that Pyrinex 480 either had low or no capacity for donating electrons or atoms.

3.3.3 Chain Breaking Acceptors

3.3.3.1 Theoretical Calculations

The ionization potential and electron affinity of each atom was calculated using vertical calculations, computed in the gas phase and with benzene and water as solvents. The electroaccepting index (Ra) was calculated based on the equations by Gázquez et al.³⁹ and Martínez et al⁴⁰ (table 3-5).

Table 3-5: The calculated electroaccepting index (Ra), with different solvents

Pesticide	Solvent	Ra
Pyrinex 480 (chlorpyrifos)	None	0.20
	Water	0.62
	Benzene	0.36
Round Up (glyphosate)	None	0.14
	Water	0.25
	Benzene	0.19

Ra values equal to one indicate a molecule is as likely to accept an electron as fluorine. Overall, Pyrinex 480 is more likely to accept electrons in any solvent than Round Up. However, these values indicate that the capacity of both species to accept electrons is low. Pyrinex 480 delays degradation by a longer time in a photo-oxidative environment compared to a thermal-oxidative environment. The difference in the thermal environment is not large for either the degradation time or carbonyl index of samples with applied Pyrinex 480 in comparison to untreated samples. Therefore, a small capacity to accept electrons is a possible explanation for the slight delay in degradation seen in a thermal environment for Pyrinex 480. The lower values obtained for Round Up suggest it will likely not accept electrons. Solvent effects for Ra increase

in comparison to the gas phase, but the pattern is conserved suggesting that Ra is not dependent on the solvent. However, to confirm this, more research is required.

3.4 Summary of Results from Different Techniques

Based on data from the above methods it was determined that Pyrinex 480 likely delays degradation through acting like a UV screener and with chain breaking acceptor capacity (figure 3-15).

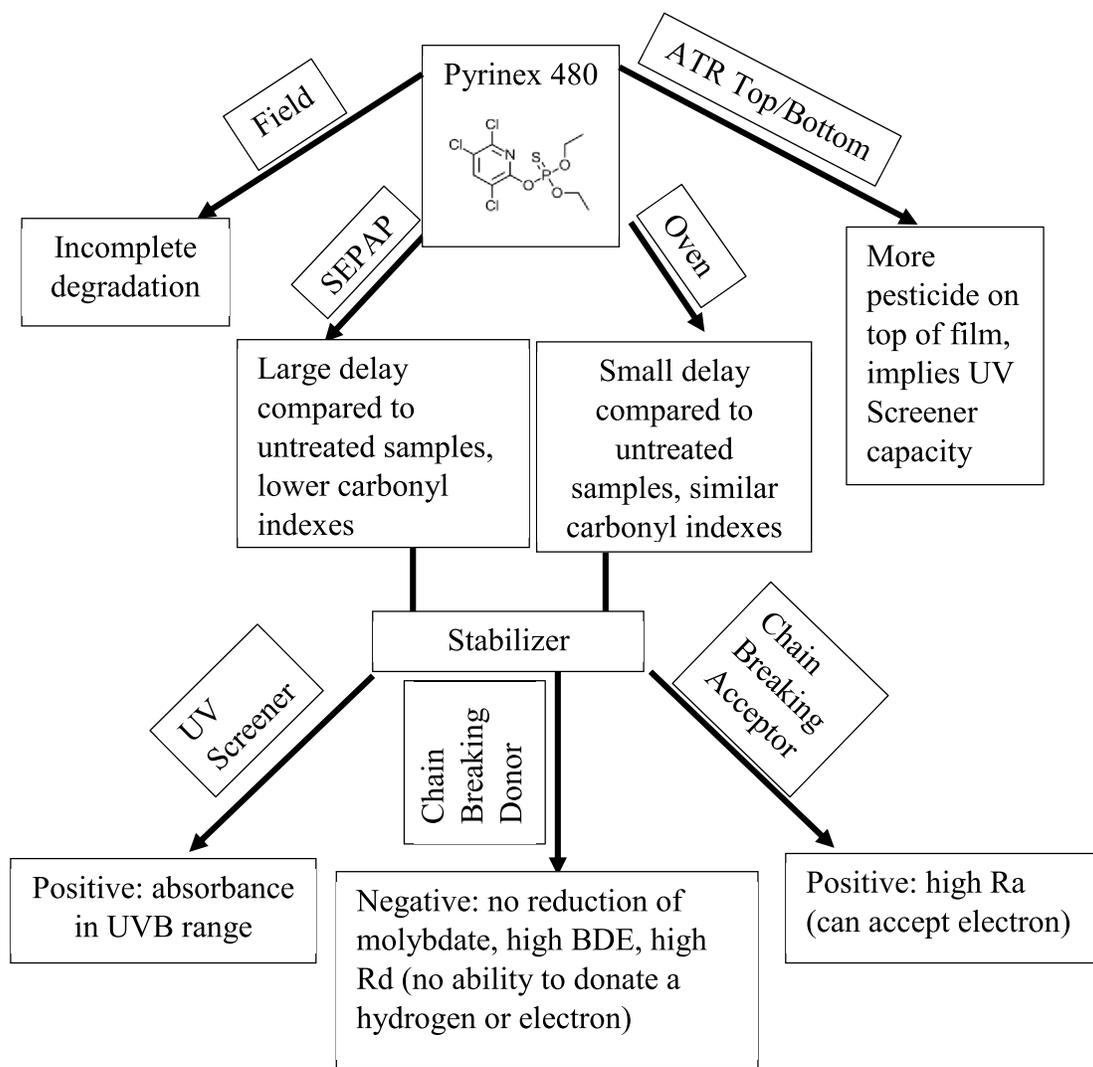


Figure 3-15: Flow chart demonstrating process of determining how Pyrinex 480 may effect degradation.

Likewise, based on data from the above methods it was determined that Round Up delays degradation through acting like a chain breaking donor (figure 3-16).

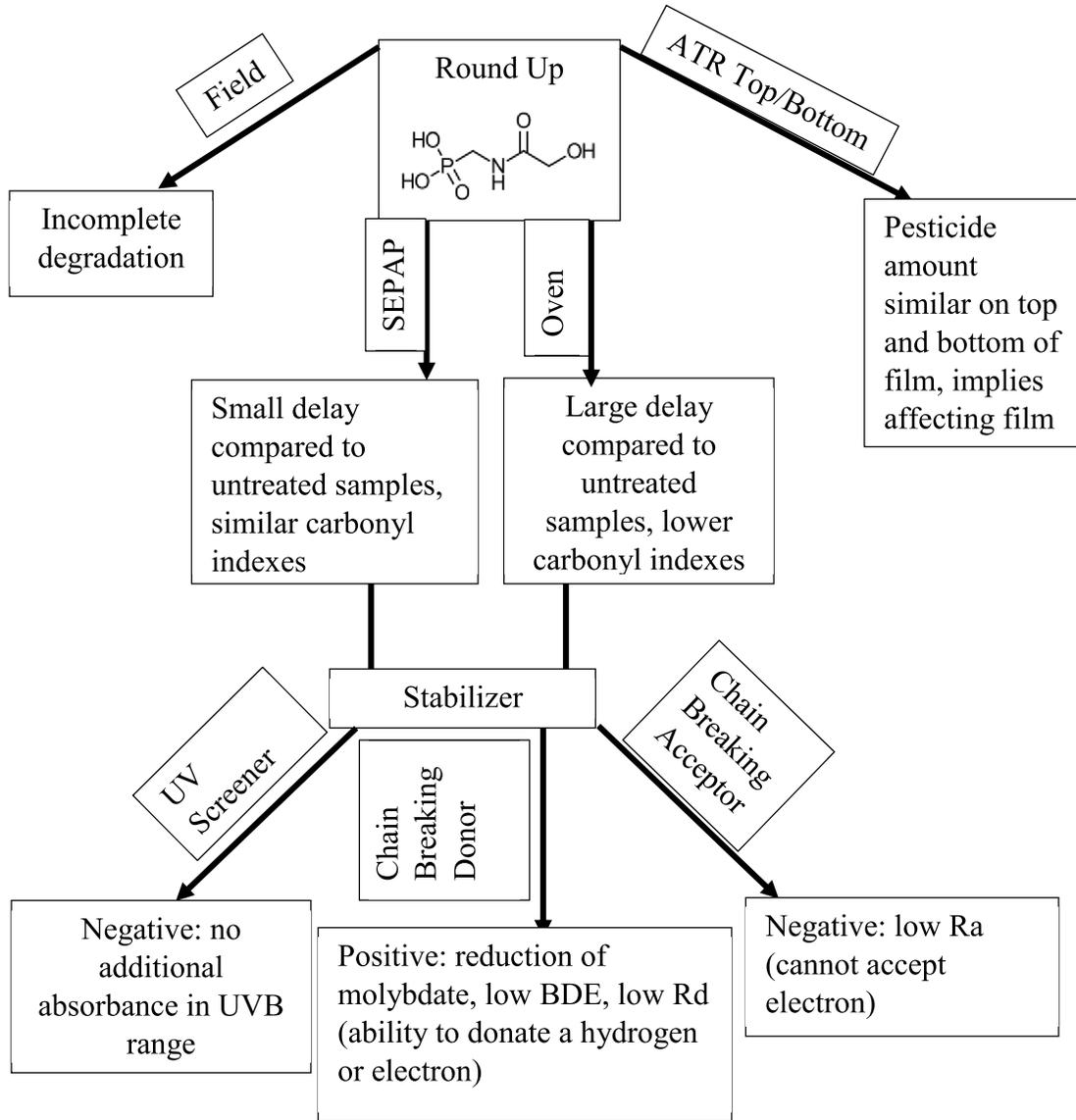


Figure 3-16 : Flow chart demonstrating process of classifying how Round Up may affect degradation.

3.5 References

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Chapter 4. Conclusions and Future Work

In spite of PE mulch films for agriculture having been the subject of research for more than 50 years, there are still many aspects of their function that remain undefined or unexplored. Though mulch films commonly come into contact with pesticides (either as part of standard agriculture practice or by accident) research regarding their interaction with PE mulch is limited. Information concerning pesticide reactions with their degradable counterparts has previously been limited to rumors derived from the users of these plastics. This study has confirmed that the effects of two common pesticides on PE film degradation are significant and attempted to quantify these effects under a number of conditions (both in the laboratory and the field environments) to define the effects of pesticides on oxobiodegradable agriculture much film.

FTIR spectroscopy was used to show that for films in a realistic field environment, in a photo oxidative accelerated degradation environment and in different well-defined accelerated thermal oxidative environments, applications of Pyrinex 480 and Round Up delayed the degradation of PE. In the field environment when films had pesticides applied to them the degradation was prevented for a minimum of one additional week, although carbonyl indices determined for field measurements suggest this delay will be much longer. Under some circumstances in accelerated conditions the delay is substantial: a delay in degradation of up to 37 % in the SEPAP device (which may be estimated to be equivalent to approximately 26 days in a temperate climate) was measured for realistic application of Pyrinex 480; application of Round Up delayed degradation in the 70 °C gravimetric oven by 52% (or 86 hours).

As the pesticides were seen to have different effects in the different exposure environments, more research was used to determine the implications of this difference. Pyrinex 480 was most effective in photo oxidative environments and less effective in thermal oxidative environments,

when the photo effects were eliminated. This suggests Pyrinex 480 stabilizes degradation by acting as a UV screener. This hypothesis was supported by further testing determining pesticide was more prominent on the top of the film after application along with the capacity of Pyrinex 480 to absorb in the UVB range. Round Up showed the strongest effect in the thermal environment and further experimental and computational testing supports the hypothesis that it stabilizes the degradation process by acting as a chain breaking donor.

In this study it was determined that pesticides can prevent the degradation in an oxobiodegradable PE agricultural mulch film. This result is significant because the films are designed to last for the lifetime of the crop planted (to decrease the risk of crop damage during harvesting) and thus any increase in the film lifetime can affect the crops harvesting schedule and yield. This research is the beginning of understanding how pesticide application can limit the controlled degradation of oxobiodegradable agriculture mulch film.

Future work in this area covers a variety of topics. First, ATR should be used to measure film samples exposed in both the field and the SEPAP to determine if there is a difference between the side of the film exposed to light and the side of the film not. This analysis may also give a better understanding of the different mechanisms that are occurring in the film, especially in regards to pesticide usage, as the reactions on the top of the film (where the pesticide is applied) may be different than the reactions on the bottom of the film. A study should also be conducted where pesticides are mixed with a surfactant to promote more uniform coverage on the film and minimize error due to patchy application.

Developing a model system for PE exposed to different environments with different stabilizers, prodegradants and pesticides may allow isolation of the different effects additives may have. As oxobiodegradable agriculture mulch films have many associated features, such as

stabilizers and thickness, a model system may also allow faster prediction of what might occur when a substance (i.e. pesticide) is added that was not planned for during processing.

Films of different thickness should also be studied to determine if the thickness of the film affects the delay in degradation. In this regard studying films of different antioxidant, prodegradant and filler composition would also help define what is occurring within the films. Also looking at different temperatures in the SEPAP would help define the dependence on temperature in a photo environment.

Although this study focused on stabilizing reactions that occur before oxidation due to smaller carbonyl indexes after pesticide application, this does not rule out additional interference at a later point in degradation between the metal prodegradants in the film and the pesticides. A NMR study determining if pesticides are forming complexes with the metals, or if the pesticides are forming functional groups with the films would be useful to further clarify how pesticides are affecting the films.

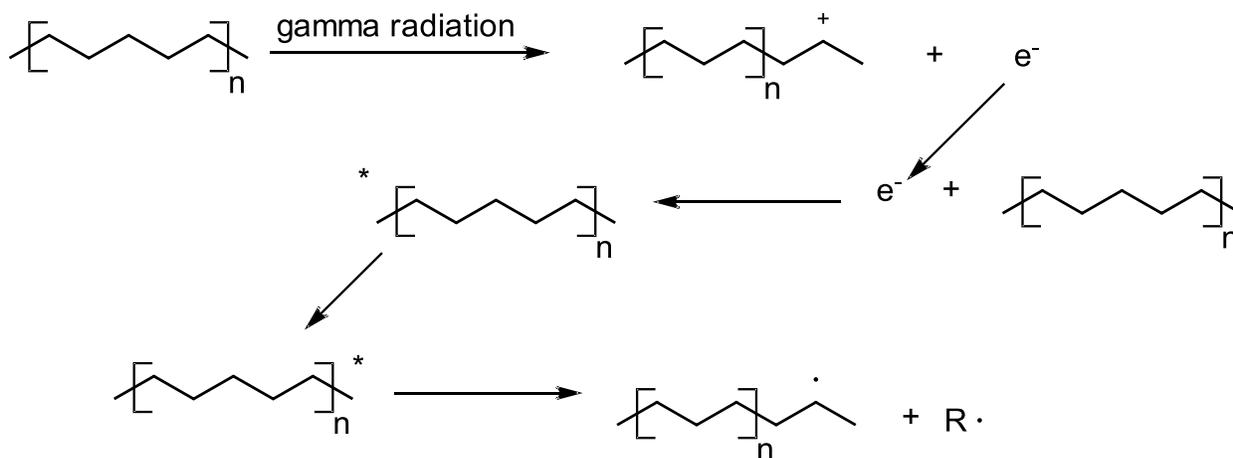
Finally, different pesticides should be explored in a laboratory and field environment, to determine if the effects seen in this study are common for other pesticides when applied to oxobiodegradable agriculture mulch films. This will also lead to more knowledge on the stabilization that is occurring from the application of pesticides, allowing the film manufactures and film purchasers to make more informed decisions on what films and pesticides to use to maximize crop growth.

Appendices

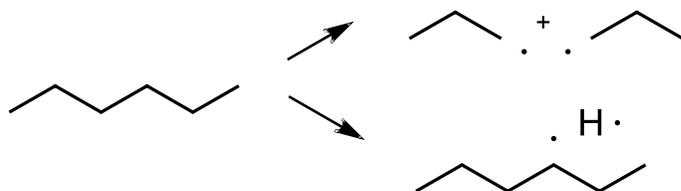
Appendix I: Detailed Mechanisms

I.1 Initiation

I.1.1 Radiation

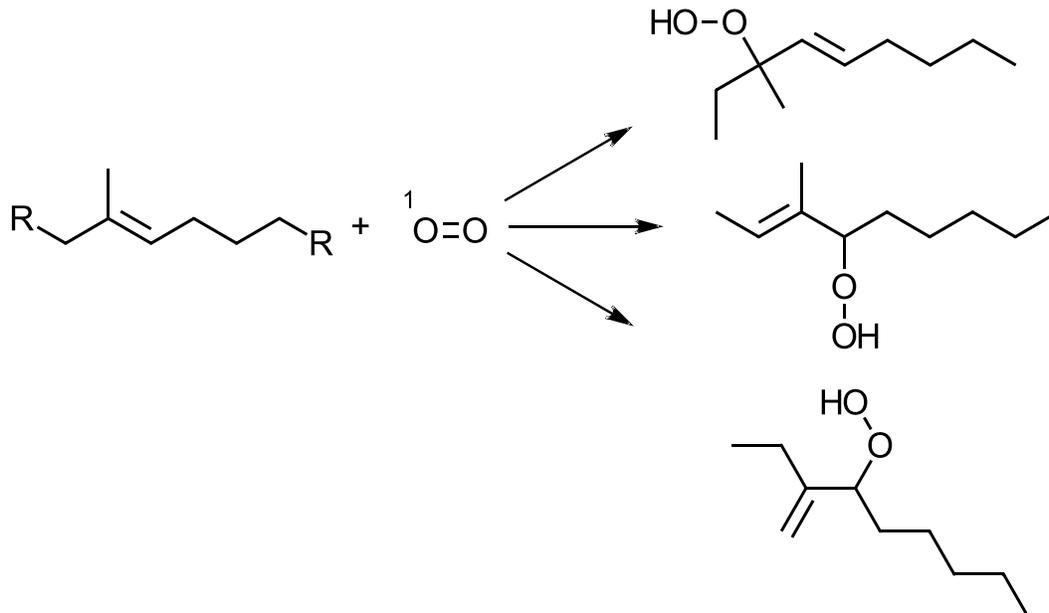


Scheme I-1: High energy breaks carbon- carbon or carbon- hydrogen bonds, rate of degradation depends on oxygen and antioxidants present; adapted from reference 1.



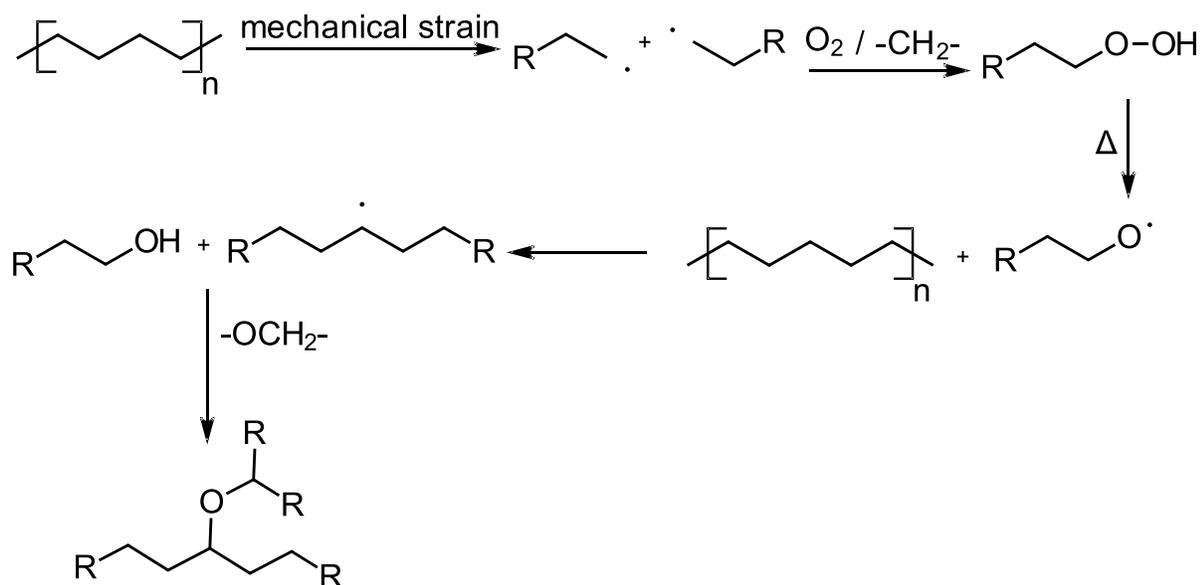
Scheme I-2: Although unlikely occasionally UV radiation may cause breakage between carbon and carbon or carbon and hydrogen bonds; adapted from reference 2.

I.1.2 Singlet Oxygen

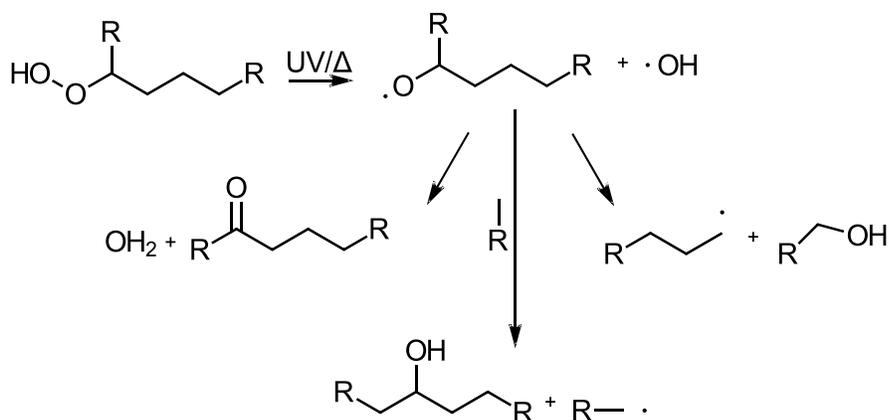


Scheme I-3: Singlet oxygen can occur from energy transfer from photo excited sensitizers; adapted from reference 3.

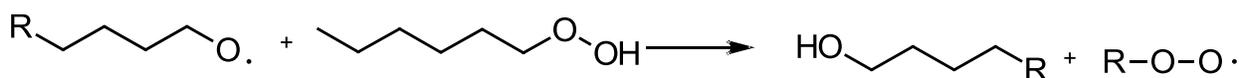
I.1.3 Shear



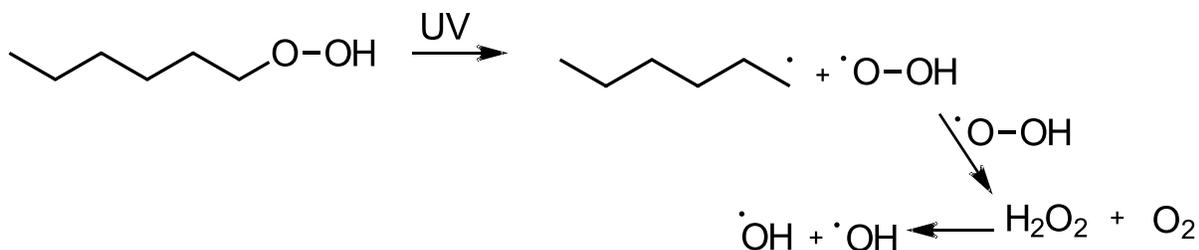
Scheme I-4: Mechanical stress in the polymer induces strain which causes crosslinking and some chain scission; adapted from reference 1.



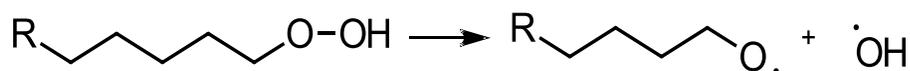
Scheme I-5: The cleavage of the hydroperoxide bond forming new functional groups or scission of the beta bond; adapted from reference 4.



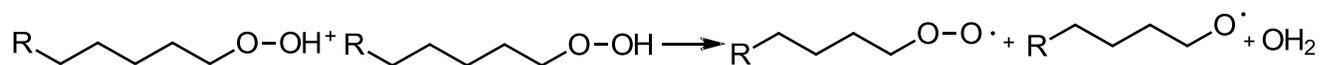
Scheme I-6: Hydroperoxides can continue to react with alkoxy radical creating a more reactive peroxy; adapted from reference 1.



Scheme I-7: Hydroperoxides can be broken into hydroperoxyl radicals. These may react to form hydrogen peroxide which can undergo photolysis to produce hydroxyl radicals; adapted from reference 3.



Scheme I-8: Low concentrations of hydroperoxides can break down into peroxy and hydroxyl groups; adapted from reference 3.



Scheme I-9: High concentrations of hydroperoxides can break down into peroxy and alkoxy groups along with water; adapted from reference 3.

I.2.2 Hydroxyl

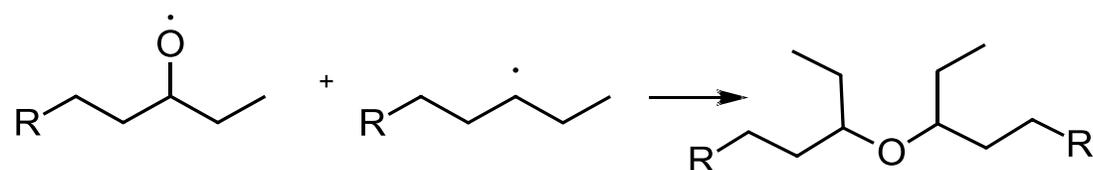
Hydroxyl radicals can occur from the breakdown of hydroperoxide³.

I.2.3 Alkoxy Radical RO*

Alkoxy radicals are created from high temperatures and pressures during processing and radiation along with hydroperoxide breakdown^{1,6}. Alkoxy radicals can react with hydroperoxides to form peroxy radicals or react with neutral polymer molecules. These reactions are in competition. The reactant with hydrogen in the alpha position that is easier to abstract will help determine which route occurs, along with the stability of the radical that will form¹.



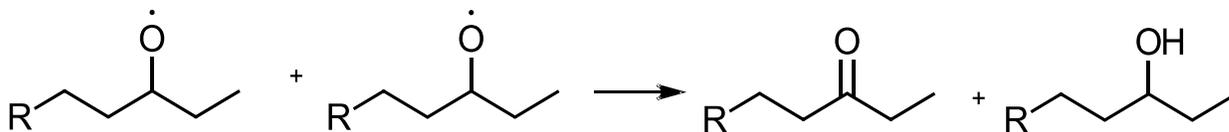
Scheme I-10: Alkoxy radicals may lead to alkyl radicals; adapted from reference 1.



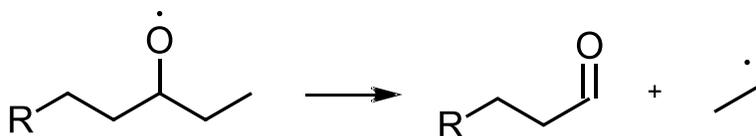
Scheme I-11: An alkyl radical reacting with an alkoxy radical causes ethers; adapted from reference 1.



Scheme I-12: Alkoxy radicals and double bonds can form a radical on the carbon atom which can continue to propagate; adapted from reference 1.



Scheme I-13: Two alkoxy radicals together may form a ketone (or aldehyde) and alcohol; adapted from reference 1.



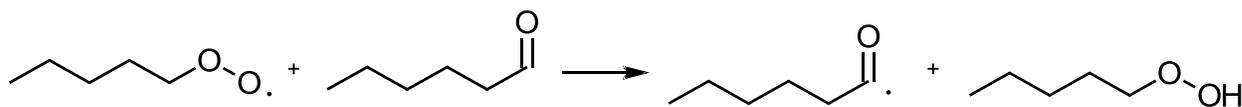
Scheme I-14: Beta scission of alkoxy radicals results in fragmentation forming an aldehyde, if crosslinking has occurred a ketone may also form; adapted from reference 3.

I.2.4 Peroxyl Radical ROO*

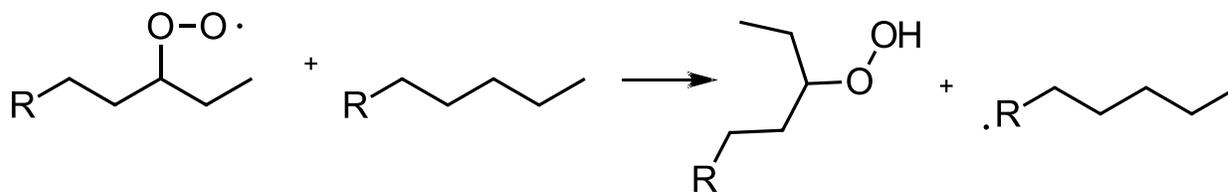
Peroxyl radicals are created from high temperatures and pressures during processing and radiation along with hydroperoxide breakdown^{1,6}.



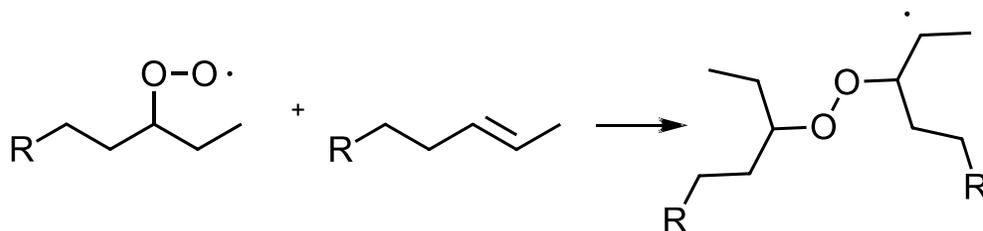
Scheme I-15: Peroxyl radicals can combine to form aldehydes (or ketones) and alcohols. Secondary peroxyl radicals are less stable than tertiary peroxy; adapted from reference 1.



Scheme I-16: Peroxyl radicals can react with aldehydes or ketones to create carbonyl radicals and hydroperoxides; adapted from reference 5.

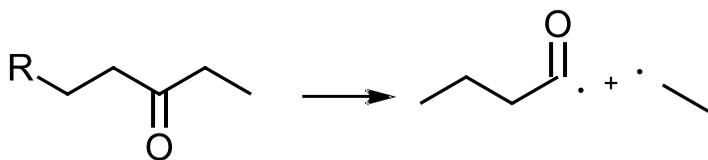


Scheme I-17: Peroxyl radicals can react with alkyl groups forming hydroperoxides and alkyl radicals; adapted from reference 1.

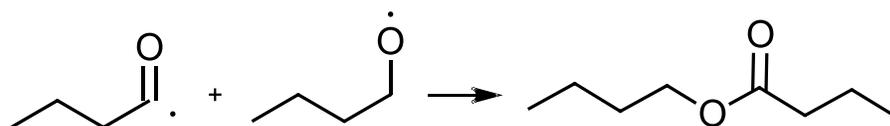


Scheme I-18: Peroxyl radicals can react with carbon-carbon double bonds forming peroxy radicals with an alkyl radical; adapted from reference 1.

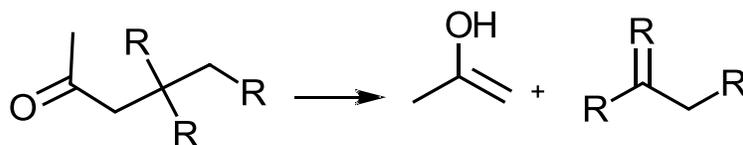
I.2.5 Ketone/Aldehyde



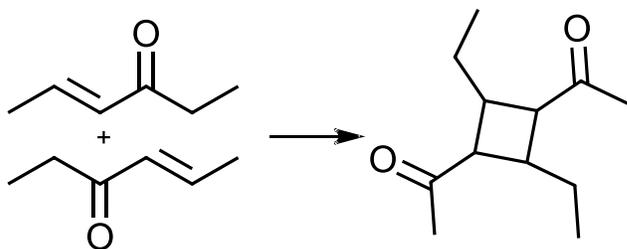
Scheme I-19: Ketones/aldehydes can break into a carbonyl and alkyl radical; adapted from reference 1.



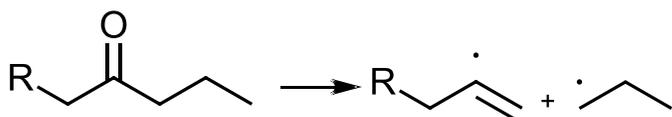
Scheme I-20: Carbonyl radicals can react with other carbonyl radicals to create esters; adapted from reference 7.



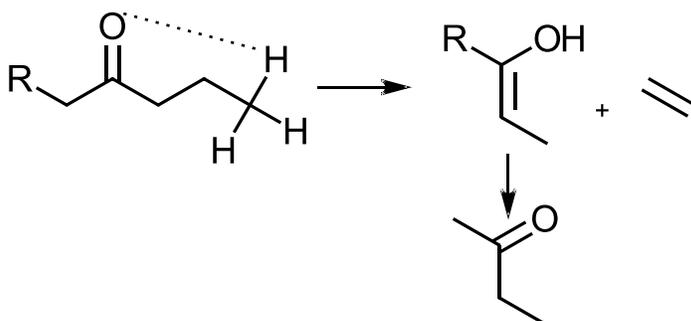
Scheme I-21: If branching occurs near a ketone or aldehyde an alcohol with a double bond and alkene may form; adapted from reference 1.



Scheme I-22: Two ketones with unsaturation may result in crosslinking; adapted from reference 3.



Scheme I-23: Norrish Type I reaction, which occurs as a result of photo-oxidative degradation; adapted from reference 7.



Scheme I-24: Norrish Type II reaction, which occurs as a result of photo-oxidative degradation; adapted from reference 7.

I.2.6 Other

Carboxylic acids can form from radicals after Norrish Type I or from aldehydes and may react further by chain scission if conditions are favourable⁸. Carbon-carbon double bonds are common by-products degradation steps and the unsaturation allows reactions to propagate.

I.3 Termination

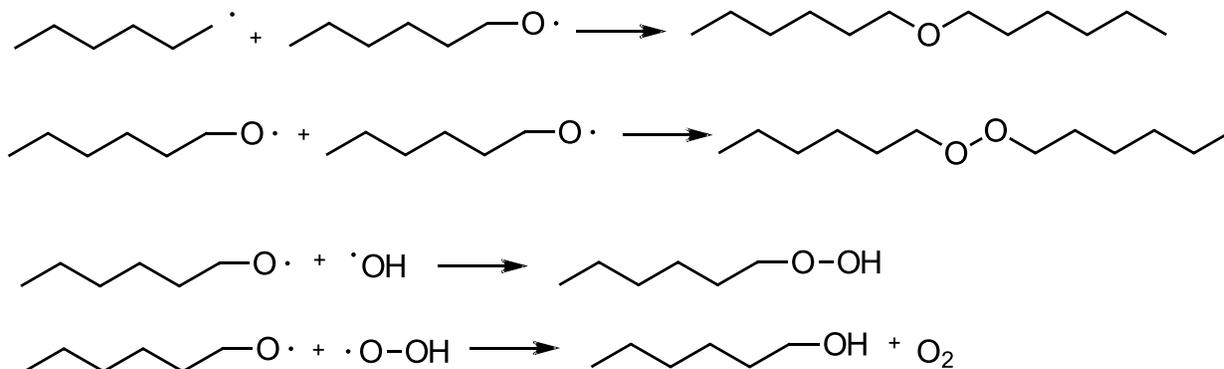
For reactions that have more than one category of reactant the reaction is only represented under one category.

I.3.1 Hydroperoxides



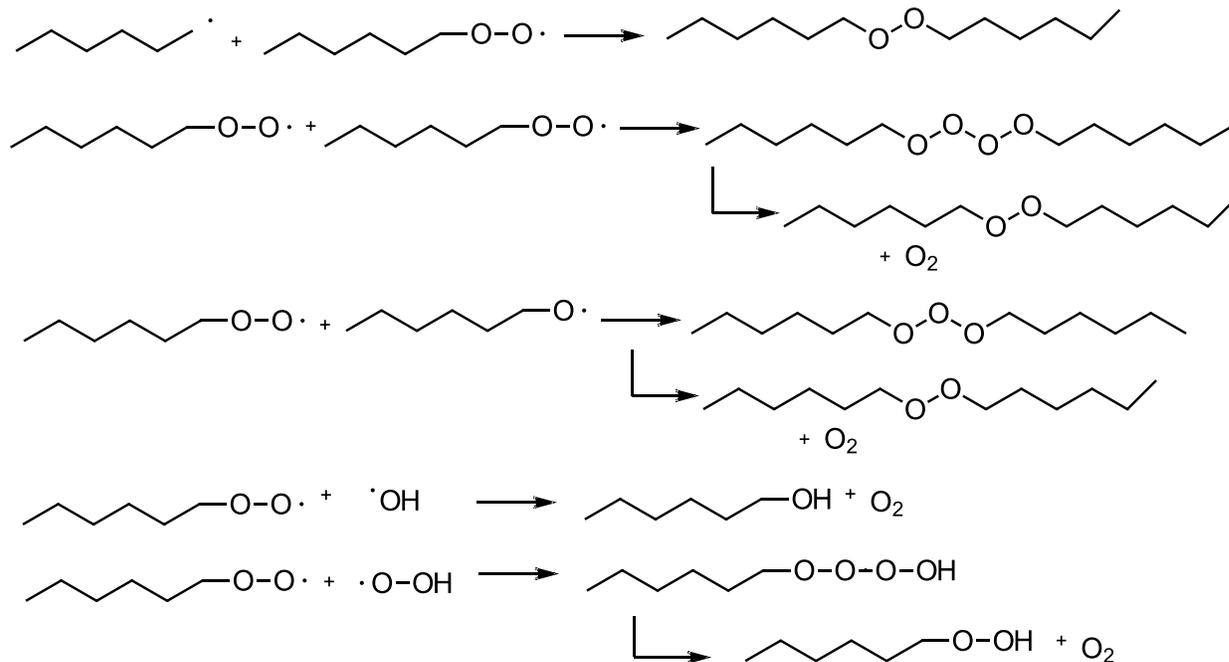
Scheme I-25: The hydroperoxides may terminate by becoming a ketone or aldehyde and water; adapted from reference 1.

I.3.2 Alkoxy radicals



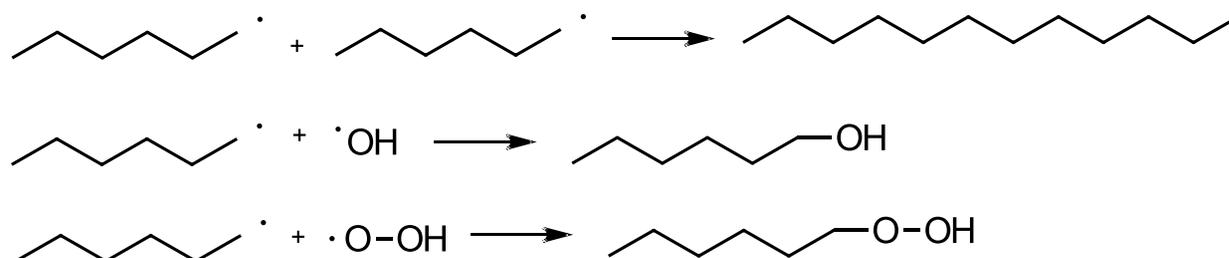
Scheme I-27: Multiple reaction pathways for termination with alkoxy to occur. Although the free radical is terminated, some species may continue to react; adapted from reference 3.

I.3.3 Peroxyl Radicals



Scheme I-28: Multiple reaction pathways for termination to with peroxyls occur. Although the free radical is terminated; some species may continue to react; adapted from reference 3.

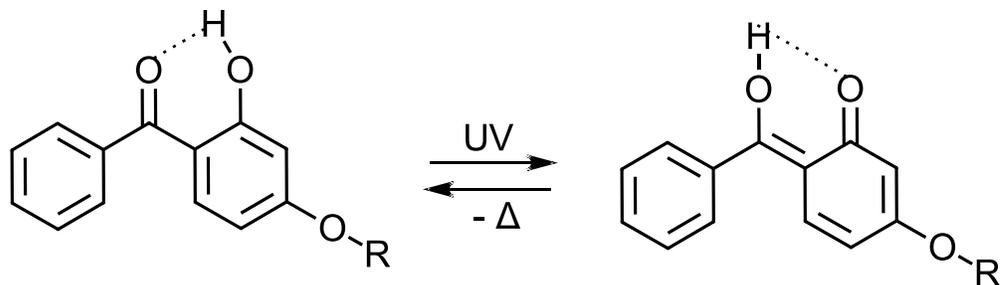
I.3.4 Alkyl radicals



Scheme I-29: Multiple reaction pathways for termination with alkyls to occur. Although the free radical is terminated, some species may continue to react; adapted from reference 3.

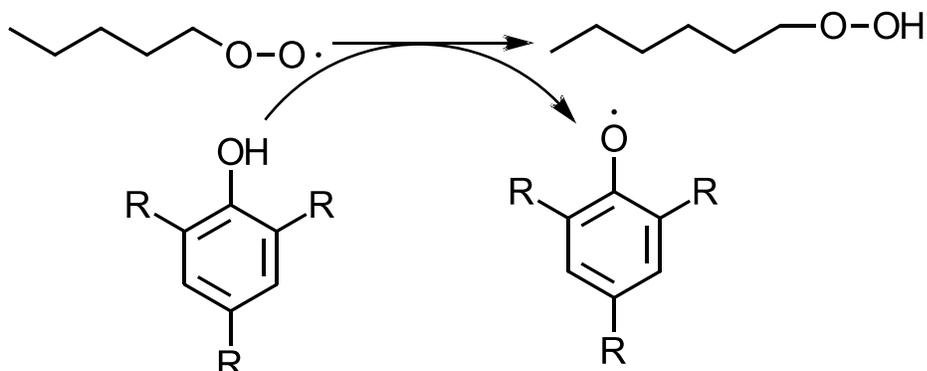
I.4 Stabilizers

I.4.1 UV Screeners

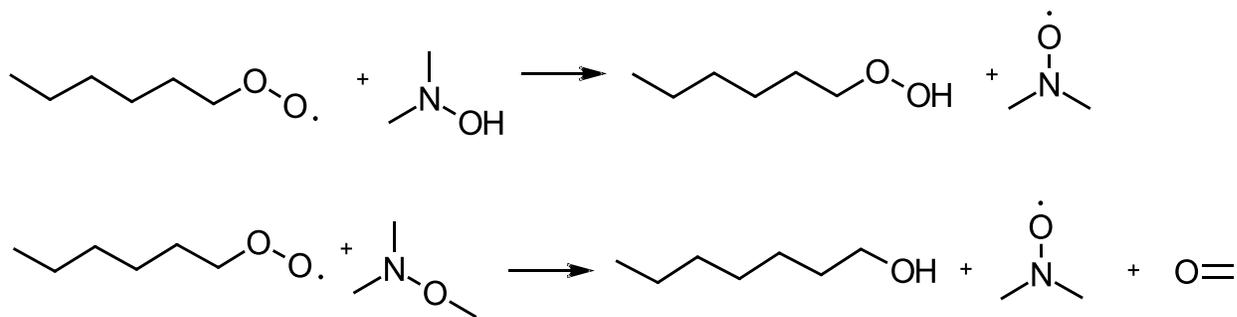


Scheme I-30: The abstraction of hydrogen from the phenol by the ketone with thermal energy loss has been seen to account for the UV screening effect; adapted from reference 1.

I.4.2 Chain Breaking Donors

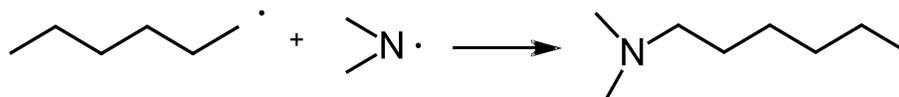


Scheme I-31: Simple example of stabilization by chain breaking donors, the radical in the antioxidant is then stabilized through resonance and/or steric hindrance or two antioxidants will stabilize each other; adapted from reference 9.



Scheme I-32: Reactions typical of hindered amine stabilizers. The formed amine radical can then take part in secondary antioxidant reactions; adapted from reference 5.

I.4.3 Chain Breaking Acceptors



Scheme I-33: The formed amine acting to stabilize an alkyl radical; adapted from reference 5.

Appendix I References

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Appendix II: Predicting the effects of different pesticides on oxobiodegradable agriculture mulch films.

Computational analysis allows the prediction of different properties of molecules based on theoretical calculations of energies from the structure of the molecule. The stabilizer capacity of pesticides can be predicted by determining whether or not pesticides have the capacity to donate or accept an atom or electron. Within this thesis it was determined that pesticides may have stabilizer capacity when applied to oxobiodegradable PE films. 15 pesticides were studied computationally to determine if they also had capacity to delay oxobiodegradation of PE films. The 15 pesticide studied computationally all have features associated with stabilizers, such as many functional and electronegative groups. Also, all of the pesticides except 1, 3-dichloropropene, glyphosate and triallate have aromatic rings indicating that they have the potential to absorb UV high enough to reach the wavelength PE absorbs at. It is therefore likely that these structures may be able to act as stabilizers.

II.1 BDE

The Bond dissociation energy (BDE) is known to represent how likely a molecule is to donate an atom¹. All calculations were performed with the Gaussian 09 code² using DFT. The BDE for every hydrogen atom bond with carbon, oxygen or nitrogen was computed unless atoms were equivalent following the method described by Leopoldini et al.¹. Each pesticide was optimized to a minimum and the frequency computed without constraints at the B3LYP^{3,4} level using the 6-311⁺⁺G(d,p)⁵⁻⁷ basis set⁶. All calculations were corrected using zero point energy. Hydrogen atom energy was set to -0.500 hartree as a precaution against the lower energy that is received for a lone hydrogen atom calculation¹. Table II-1 shows the lowest calculated BDE.

Table II-1: The energy for the BDE of hydrogen in each pesticide computationally tested.

Pesticide	Lowest BDE for Hydrogen kJ/mol
1,3- Dichloropropene	336.9
2,4 – D	343.9
Atrazine	366.4
Bromoxynil	354.6
Chlorpyrifos	397.2
Chlorothalonil	NA
Dicamba	392.9
Dimethenamid	346.0
Ethalfuralin	424.1
Glyphosate	302.1
MCPA	345.3
Mecoprop	342.4
R-Metolachlor	367.3
S-Metolachlor	334.9
Triallate	346.4

Polyphenol molecules that are expected to have strong antioxidant capacity have been calculated to have BDE of less than 350 kJ/mol¹. Pesticides in this study were calculated between 302.1 and 424.1 kJ/mol. Therefore the BDE calculations indicate the majority of the pesticides considered could donate a hydrogen atom to stabilize a radical reaction, acting as a reducing agent with similar capacity to common antioxidants.

Based on the lowest BDE values, the most likely pesticide to donate a hydrogen to a radical reaction is glyphosate. S-metolachlor, 1, 3-dichlorpropene, mecoprop, 2, 4-D, MCPA, dimethenamid and triallate also have low BDE energies that might indicate hydrogen donating capacity. The remaining pesticides have higher BDE suggesting that they would be less likely to donate a hydrogen. Mecoprop, 2, 4-D, MCPA, dimethenamid and triallate are all very close in regards to BDE, within 5 kJ/mol of each other suggesting that these five pesticides would have similar capacity to donate a hydrogen atom.

II.2 Electrodonating and Electroaccepting

A previous study by Gázquez et al.⁹ provided a method of calculating the electrodonating and electroaccepting power of molecules. The ionization potential and electron affinity of each molecule was calculated using vertical calculations, computed in the gas phase and with benzene and water. The electrodonating index (Rd) and electroaccepting index (Ra) were calculated based on the equations by Gázquez et al.⁹ and Martínez et al.¹⁰ in the gas phase and with solvation effects of benzene and water (table II-2).

Table II-2: Calculated Ra and Rd values, rounded to the nearest hundredth.

Pesticide	Solvent	Ra	Rd
1,3 – Dichloropropene	None	0.11	1.35
	Water	0.39	1.58
	Benzene	0.67	1.84
2,4-D	None	0.14	1.33
	Water	0.40	1.54
	Benzene	0.23	1.39
Atrazine	None	0.11	1.22
	Water	0.41	1.51
	Benzene	0.18	1.24
Bromoxynil	None	0.2	1.46
	Water	0.6	1.78
	Benzene	0.36	1.6
Chlorpyrifos	None	0.20	1.39
	Water	0.62	1.84
	Benzene	0.36	1.56
Chlorothalonil	None	0.48	2.03
	Water	1.06	2.48
	Benzene	0.70	2.17
Dicamba	None	0.15	1.31
	Water	0.27	1.44
	Benzene	0.29	1.44
Dimethenamid	None	0.11	1.18
	Water	0.40	1.46
	Benzene	0.20	1.25
Ethalfuralin	None	0.49	1.86
	Water	1.51	2.82
	Benzene	0.86	2.20
Glyphosate	None	0.14	1.34
	Water	0.25	1.30
	Benzene	0.19	1.32
MCPA	None	0.11	1.19
	Water	0.31	1.45
	Benzene	0.16	1.04
Mecoprop	None	0.11	1.17
	Water	0.28	1.27
	Benzene	0.17	1.18
R- Metolachlor	None	0.13	1.25
	Water	0.63	1.57
	Benzene	0.31	1.29
S-Metolachlor	None	0.12	1.25
	Water	0.30	1.38
	Benzene	0.19	1.28
Triallate	None	0.13	1.24
	Water	0.37	1.47
	Benzene	0.21	1.29

None of the pesticides studied had R_d values less than one indicating that the pesticides would not be as good of electrodonor as sodium is. However, values close to one were obtained for most of the pesticides indicating a possibility of donating electrons. Glyphosate, mecoprop, MCPA, atrazine, dimethenamid, R, and S-metolachlor, and triallate are the most likely candidates based on the lowest R_d values.

Only when water was used as a solvent were there any R_a values greater than one. This suggests that some of the pesticides could accept electrons, but they would not be as good electron acceptors as fluorine. Due to the overall low values for R_a it is likely that only ethalfluralin, chlorothalonil, chlorpyrifos, and bromoxynil would be able to accept electrons.

Based on theoretical calculations it is likely that all of the pesticides studied would delay degradation if they were applied to oxobiodegradable mulch film.

Appendix II References

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