

ABSTRACT

VISWANATH, VIDYA. Degradation Studies of Polypropylene Fibers and Nonwovens with Prodegradant Additives. (Under the direction of Dr. Richard Kotek).

The purpose of this research is to investigate an inexpensive pro-oxidant and pro-degradant additive system that can be applied during melt processing to produce biodegradable polyolefin-based (PP) nonwovens. The first phase of this research dealt with polypropylene filaments with pro-degradant additives. PP filaments with TDPA™ and ECM MasterBatch Pellets™ additives were spun and characterized for their physical and chemical properties after xenon arc lamp exposure. Tensile studies showed significant loss of elongation and tenacity in additive containing samples on xenon arc lamp exposure. IR studies confirmed the formation of carbonyl compounds marked by an increase in carbonyl and hydroxyl index thereby indicating the occurrence of photooxidation of polypropylene.

The second phase of the research involved the production of spunbond polypropylene nonwovens with TDPA™ and ECM MasterBatch Pellets™ additives. These nonwovens were subjected to 3 types of degradation i. e. abiotic conditions of xenon arc lamp exposure and biotic conditions of vermicomposting and soil burial and subsequently characterized for their physical and chemical properties. Xenon arc lamp exposed nonwovens showed a drastic reduction in tensile strength (peak load) as compared to vermicomposted and soil buried samples. IR studies confirmed the occurrence of bio-chemical degradation having occurred in soil buried samples. It can be inferred that degradation of polypropylene filaments and nonwovens with additives depends on various factors like the additive type (TDPA™ or ECM MasterBatch Pellets™) or the amount of the additive used, type and nature of degradation carried out (abiotic or biotic)

Degradation Studies of Polypropylene Fibers and Nonwovens with Prodegradant Additives

by
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DEDICATION

Dedicated to my family for their unconditional love, support and moral
encouragement.

BIOGRAPHY

Vidya Viswanath was born in Mumbai, India. She completed her Bachelor of Technology, in Textile Technology from Veermata Jijabai Technological Institute (V.J.T.I.) , Mumbai in 2007. After completing her under graduation, she obtained professional experience as a Technical Engineer at BASF India Limited, Mumbai. She came to the United States to pursue a Master of Science degree in Textile Engineering at North Carolina State University in Fall 2008.

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SECTION 1- LITERATURE REVIEW

1. 1. MOTIVATION AND OBJECTIVES

PP fiber is one of the most successful commodity fibers, reaching a world production capacity of four million tons a year. PP fibers belong to the newest generation of large-scale, manufactured chemical fibers, the fourth largest volume in production after polyesters, polyamides and acrylics [1-2].

During last decades, the great population increase worldwide together with the need of people to adopt improved conditions of living led to a dramatic increase of the consumption of polymers (mainly plastics).

Polyolefins [Low density polyethylene (LDPE), High density polyethylene (HDPE), Polypropylene (PP)] are a major type of thermoplastic used throughout the world for applications like bags, toys, containers, pipes (LDPE), house wares, industrial wrappings and film, gas pipes (HDPE), film, automotive parts, battery cases, and electrical components (PP).

In 2004, 1.85 million tons of melt blown/ spunbond nonwovens products were produced in the world. Of these 1.45 million tons was the share of polypropylene raw material (79%). [3]. This shows that the waste generated from the nonwovens industry has increased gradually every year.

Factories that manufacture nonwovens normally dispose of the selvages by burying and burning, often leading to environmental pollution and destruction. It is surprising to note that these wastes are not recycled, but incinerated or disposed in landfills, where it takes

more than 100 years to degrade. Recycling and reusing fibrous waste is one of the most important environmental tasks that face the world, to reduce environmental loading and promote the most effective use of resources.

This is more so in the case of polyolefins, which are high molecular weight polymers.

Due to their high molecular weight, they are unable to enter the body of micro organisms easily and hence are not easily biodegradable. Their basic structure comprises carbon and hydrogen, due to which they are usually inert. Their hydrophobic nature prevents the growth of microorganisms on them thereby inhibiting the enzymatic action of microorganisms. The large accumulation of these thermoplastic materials in the environment is an issue of increasing concern from the point of view of environmental safety. Thus there is an increasing need to develop polyolefin fibers with increased biodegradability, which can be further made into nonwoven products for use in products like face masks, filters, wipes etc.

One approach to achieving this is to spin fibers using some pro-oxidant additives during the melt spinning of polypropylene. It is known that the oxidation of polyolefins yields low molecular weight oligomers which are conducive environments to the growth of microorganisms due to their hydrophilicity. These can further help to break the oligomers into carbon dioxide and water.

Thus the primary objective of this research is to develop an inexpensive pro-oxidant and pro-degradant additive system that can be applied during melt processing to produce biodegradable polyolefin-based (PP or PE) fibers and nonwovens.

1. 2. INTRODUCTION

1.2.1. Polypropylene and its properties

Stereoregular polypropylene (PP) was discovered in the early 1950s by Giulio Natta.

Polypropylene's repeating unit is $-\text{[CH}_2\text{-CH(CH}_3\text{)]}_n-$. It is a thermoplastic polymer obtained by the polymerization of propylene in the presence of a catalyst under controlled heat and pressure. The molecular configuration of PP can be altered to give three types of PP depending on the catalyst and the polymerization method used namely atactic, isotactic, and syndiotactic configurations [4, 5].

PP has attracted much attention because of the superior properties that it offers at low to moderate costs. These advantages include:

- 1) high toughness
- 2) high strength to weight ratio
- 3) lighter weight
- 4) corrosion resistance
- 5) chemical resistance.

Due to easy processability PP has replaced conventional materials like wood, metal and glass as an efficient as well as cost effective material for the manufacture of articles with various colors, complicated shapes, and designs [6, 7].

The properties of textile grade polypropylene are enlisted in Table 1 below:

Table 1. Properties of textile grade polypropylene [8].

Tensile Strength (gf den-1)	3.5-5.5
Elongation at break (%)	40-100
Abrasion Resistance	Good
Moisture Absorption (%)	0-0.05
Elastic Recovery (after 30 s at 2% elongation)	
Immediate (%)	91
Delayed (%)	9
Glass Transition Temperature (°C)	-15 to -20
Softening Point (°C)	140
Melting Point (°C)	165
Chemical Resistance	Generally excellent
Relative Density	0.91
Thermal Conductivity	6.0 (with air as 1.0)
Pyrolytic Stability (°C)	350
Electrical Insulation	Excellent
Resistance to Mildew, Moth	Excellent

1.2.2. Melt spinning processing of PP fibers

Melt spin processing first began in 1940 with the commercial production of nylon 66. It dominates all other fiber manufacturing processes like wet spinning, dry spinning etc due to its efficiency in producing high quantity and quality fibers, thereby making it a very cost effective process. Melt spin processing begins with the feeding of polymer pellets or chips from a hopper into the extruder as shown in Figure 1.1.

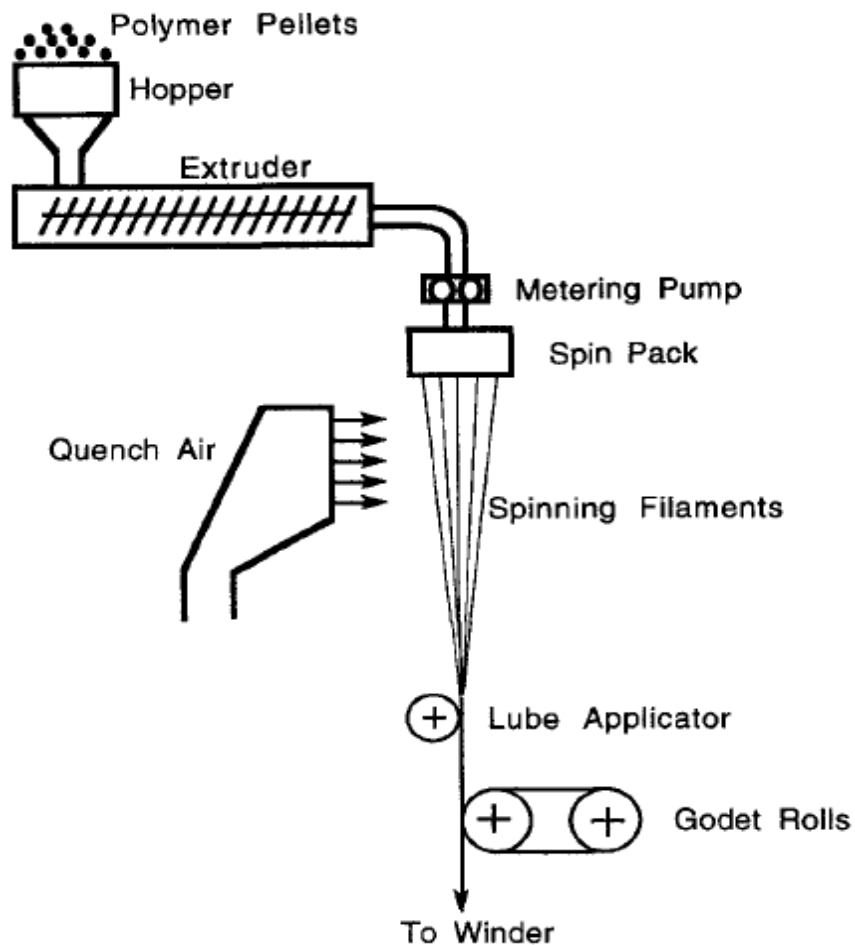


Figure 1.1. Schematic of the melt spinning process [9].

The extruder is available in different configurations and may comprise a single or twin screw. This screw is enclosed in a barrel and is used to melt the polymer pellets and transport the melt along the length of the barrel under pressure. The pellets melt due to the heating of the screw and barrel as well as due to the mechanical shearing of the polymer during its travel through the barrel. The viscosity of the polymer during processing is a function of its molecular weight and the temperature and pressure within the system. The shear rate also affects the viscosity of the polymer. As the shear rate increases, the viscosity of the polymer decreases and shear thinning occurs.

The polymer passes through a pre-filter before entering the spinning head. Pre-filtration helps to remove partially degraded polymer gels, foreign impurities such as metal particulates, and gaseous bubbles. A filter pack is made from a set of selected screens, one laying on top of another. Such a pack could be a top screen of 50 mesh followed by a 150 mesh, then a 320 mesh and finally a 50 mesh on the bottom. Some such are combinations are either loose or tack welded together. Most are woven wire, some are non-woven sheets of sub-micrometal filaments and some are even stamped-out centered metal discs. Most filter elements are made of some type of stainless steel. The polymer melt passes through these filters and finally reaches the spinneret [99]. The spinneret is a metal plate, 3-30 mm thick with various size holes (usually 100-500 micrometers) that influence the size and shape of the spun fibers [8].

On being extruded from the spinneret, the moving jet experiences die swell i.e. the polymer recovers its stored elastic energy on being released from the high-pressure zone

of the spin pack. The moving jet is then quenched in a cooling chamber, cooled and then solid fiber is wound onto a package.

1.2.3. PP applications for nonwovens

Among the textile applications, nonwovens are one of the fastest-growing segments of the textile industry and constitute roughly one-third of the fiber industry.

Because of its high performance to cost ratio, PP fiber finds extensive use in the nonwovens industry. PP is a very important fiber in nonwoven processing and dominates in many nonwoven markets. The main application areas include: nonwoven fabrics, particularly absorbent product coverstock markets, home furnishings and automotive markets.

The applications of spunbonded nonwovens in particular, include disposable and durable products. In the automobile industry, these nonwovens are abundantly used for interior door panels, seat covers, automobile carpet backings etc.

Filtration clothing, medical wraps, gowns, health and hygiene products are some areas in medical textiles where spunbond nonwovens are regularly used.

Spunbonded geowebbs play an important role in geotextiles used to prevent soil erosion, protect canals and reservoirs, etc. Applications in packaging materials include medical sterile packaging, envelopes, food packaging containers etc.

1.2.4. Manufacturing process for producing spunbond nonwovens

The spunbonding process has been defined as a manufacturing system involving

direct conversion of a polymer into continuous filaments, integrated with the conversion of filaments into a random-laid, bonded nonwoven [10]. A spunbonded nonwoven is a fabric formed by filaments that have been extruded, drawn, laid on a belt, and bonded thermally, chemically or mechanically.

The spunbonding process includes 5 operations as listed below:

- a) Filament extrusion,
- b) Drawing,
- c) Quenching,
- d) Lay down,
- e) Bonding.

A sketch of Hill's open spunbond process with a belt collector is depicted in Figure 1. 2

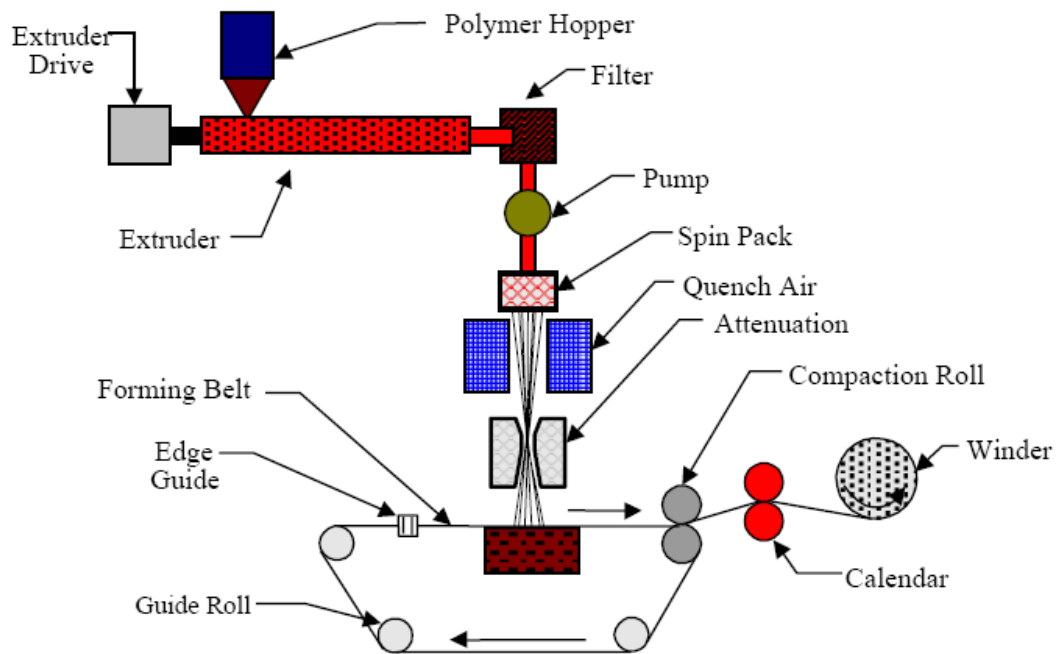


Figure 1.2. Diagram of the open spunbond process with belt collector [11].

The polymer is fed to an extruder in either pellet or powder form. In the extruder, the polymer can also be mixed with additives, color master batch, stabilizers etc. As the polymer passes through the extruder, it is subjected to heat, mechanical action and viscous flow due to which it melts. Sometimes, vented twin-screw extruders are used to dry the polymer as it melts. This molten polymer under pressure, is then conveyed to a filter. The main function of the filter is to separate the molten polymers from foreign particles, such as metals, solid polymer impurities, etc. Post filtration, the polymer melt is fed to a metering pump. This pump, which is generally a constant volume device, helps to pump out molten polymer at a fixed rate to ensure precise pumping of the molten polymer. The melt pumps help to provide high pressure for the spin pack. The molten polymer then passes from the gear pump to a spin beam, which includes the feed distribution system. This feed distribution system helps to provide uniform flow of polymers to a die block assembly (spin pack). The die assembly consists of a polymer feed distribution and a spinneret. From the feed distributor, the polymer melt enters the spinneret. The spinneret is a single metal block having several thousand orifices, which are usually circular or rectangular in shape. Usually in commercial production lines, several groups of spinnerets (blocks) are used to increase the coverage of fibers. On emerging from the spinneret holes, they are directed downwards into a quench zone or quench chimneys. As they travel through the quench zone, cool air is directed across the filament bundle to cool the molten filaments and thereby causing them to solidify. After being attenuated and quenched, the filaments are deposited on a moving belt. The vacuum under the belt assists in the formation of the filament web on the forming belt

and in removing the air used in the extrusion/drawing operation. Compaction rolls could also be used to increase the cohesion between filaments and provide integrity to the web.

Finally, this continuous filament web is delivered to a bonding section, where loose filaments are bonded into a strong integrated fabric by usage of bonding techniques like calendaring, needle punching, hydroentangling, chemical bonding etc. The spinning speeds of the spunbonding can range from 1,000 to 8,000 m/min, depending on the processing polymer characteristics, desired properties of resulting fiber, and process productivity [12]. PP does not show significant improvement in the molecular orientation with an increase in the spinning speed due to its high crystallizing ability [13]. Thus, PP usually is spun at about 2000 m/min.

1.2.5. Need for biodegradability

It has been observed that the nonwoven industry in general is dominated by synthetic fibers. As shown in the Figure 1. 3 and 1. 4 below, polyester and polypropylene continue to dominate this market [14].

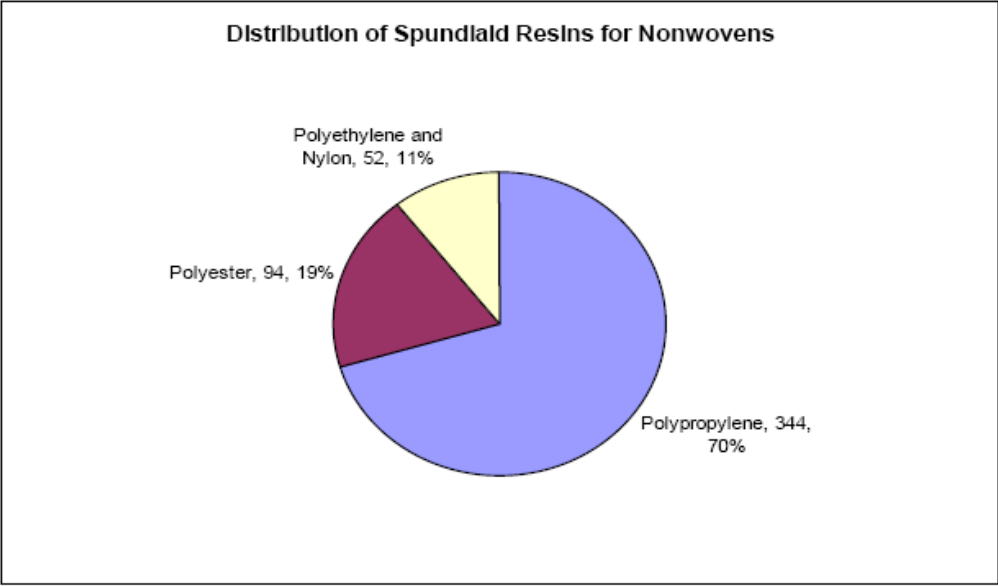


Figure 1.3. Spunlaid resin distribution: Analysis of the nonwovens industry in North America 2003-2008 by INDIA [14].

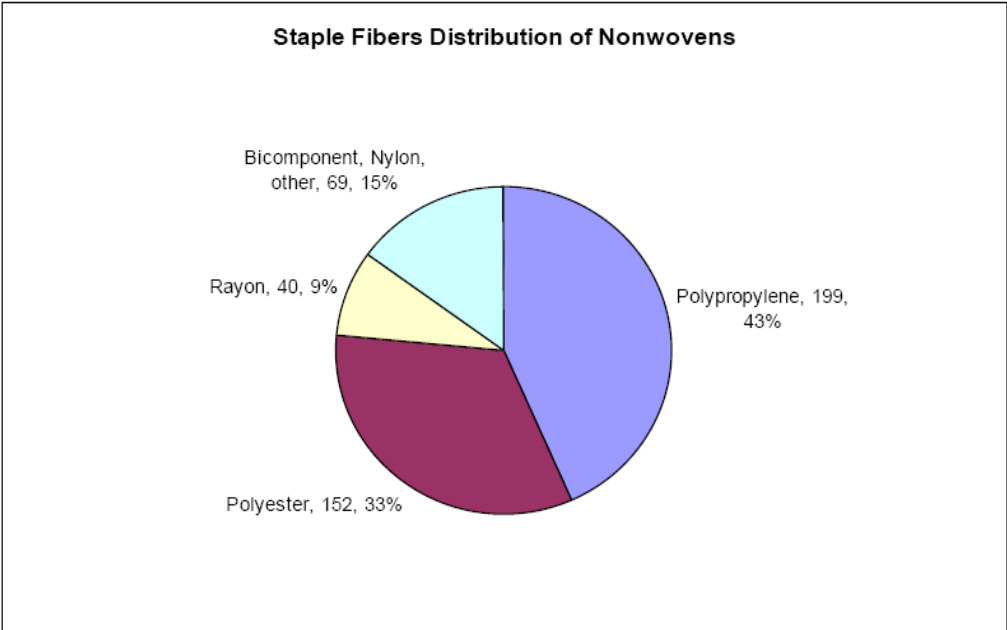


Figure 1.4. Staple fibers distribution: Analysis of the nonwovens industry in North America 2003-2008 by INDIA [14].

Since the duration of life of plastic products is very small (roughly 40% have duration of life smaller than 1 month), there is a vast waste stream (approximately 21.2 million tons for 2003) that reaches each year to the final recipients creating a serious environmental problem (15).

Waste disposal is now becoming a major concern because of the scarcity of acceptable waste disposal sites accompanied by an increasing amount of waste. Plastics comprise about 18% of municipal solid waste and are among the most visible and the least degradable (16).

Though these plastics can be recycled, a vast majority of these are disposed in landfills where they accumulate due to their resistance to degradation and hence are a cause of environmental concerns. Thus there is an increasing need to develop products from plastics which degrade easily in composting and landfill conditions.

One aspect of making polymers that are eco friendly would include usage of bio-based polymers which are commonly referred to as biopolymers. These are synthesized from renewable resources plant and animal origin instead of non renewable resources like petroleum. These include polyglycolic acid, polylactic acid (PLA), and polycaprolactone, polyhydroxyalkanoates (PHA) etc.

For example, PLA is made by breaking down the starch in corn, sugarcane, sweet potatoes, and other plants to produce glucose that is then fermented to produce lactic acid. This lactic acid can be polymerized and converted into PLA. Synthetic aliphatic polyesters, which are synthesized from diols and dicarboxylic acid via condensation polymerization, are known to be completely biodegradable in soil and water.

However, the problem with these biopolymers is that they do not have mechanical and thermal properties sufficient to fully replace common polymers. Bioresins usually cost two or three times as much as petroleum based resins and often lack the required strength and durability. [17-18]

The other approach to making ecofriendly polymers is to develop biodegradable plastics. This can be done by the usage of additives or blends that accelerate the degradation of these plastics. This is fundamentally the approach of this research project. The primary objective of this research is to develop an inexpensive pro-oxidant and pro-degradant additive system that can be applied during melt processing to produce biodegradable polyolefin-based (PP or PE) fibers and nonwovens.

1.3. DEGRADATION MECHANISMS OF POLYPROPYLENE

Degradation of components made from polymeric materials occurs in a wide variety of environments and service conditions, and very often limits the service lifetime (19). In broad terms, the majority of failures which are the consequence of polymer degradation can be attributed to one of three types of degradations: *Molecular degradation* which may be caused during processing, usually due to elevated temperatures (as in melt spinning) and often in combination with an oxidizing atmosphere, *Environmental degradation* i.e. degradation in service caused by the natural environment , *Chemical degradation* i.e. attack by an aggressive chemical, during the lifetime of the product.. In the case of polyolefins in particular, photooxidation is a major source of degradation.

1.3.1. Photodegradation

Photodegradation refers to the degradation of polymer by the action of ultraviolet light (UV) from the sun with a wavelength of 290–400 nm [20]. This is especially important for the products that comprise litter on the ground or which float on water. Such litter is most objectionable since it is visible and sometimes causes problems for fauna.

Most polymers do not have good UV stability and thus it is necessary to add carbon black, TiO₂, benzophenone, benzotriazole, Hindered Amine Light Stabilizers (HALS), and other stabilizers to provide adequate retention of properties during the expected life of the product. Therefore, with some polymers it may be possible to obtain the desired degradation by merely reducing or eliminating such additives.

To obtain adequate photodegradation, most polymers need to be modified during synthesis or post treatment by the insertion of photo chemically active groups. Addition of pro-oxidants such as metal salts [21-22], carbonyl functionality [23-24], external photosensitizers and, ketones, ethers, thiols, and polyunsaturated compounds [19] into the polymer main chain or side chain, are examples that can lead to trigger a chain reaction that breaks the bond between the molecules.

Degradation is evidenced by a decrease in molecular weight; the weight average molecular weight being inversely proportional to the amount of radiation received [25]. This lower molecular weight polymer is broken up into smaller particles by physical forces in the environment to a point where microorganisms are capable of transporting and metabolizing them.

Bolland and Bateman have assumed that the photooxidation of polypropylene to be a free radical chain mechanism similar to that formulated by for the thermal oxidation of hydrocarbons in the liquid phase [26-27].

In general, the photooxidation of polypropylene is initiated by the abstraction of hydrogen atom preferably tertiary hydrogen by free radicals formed from the decomposition of impurities such as hydroperoxide formed during processing [28]. The photodegradation of PP would not occur without these initiating centers because polyolefin polymer does not absorb UV-radiation in the solar spectrum at the earth surface [29] but once initiated the chemical degradation takes place through an autocatalytic process that is diffusion controlled [30]. The photooxidation mechanism of polypropylene can be summarized in Figures 1.5, 1.6 and 1.7 respectively

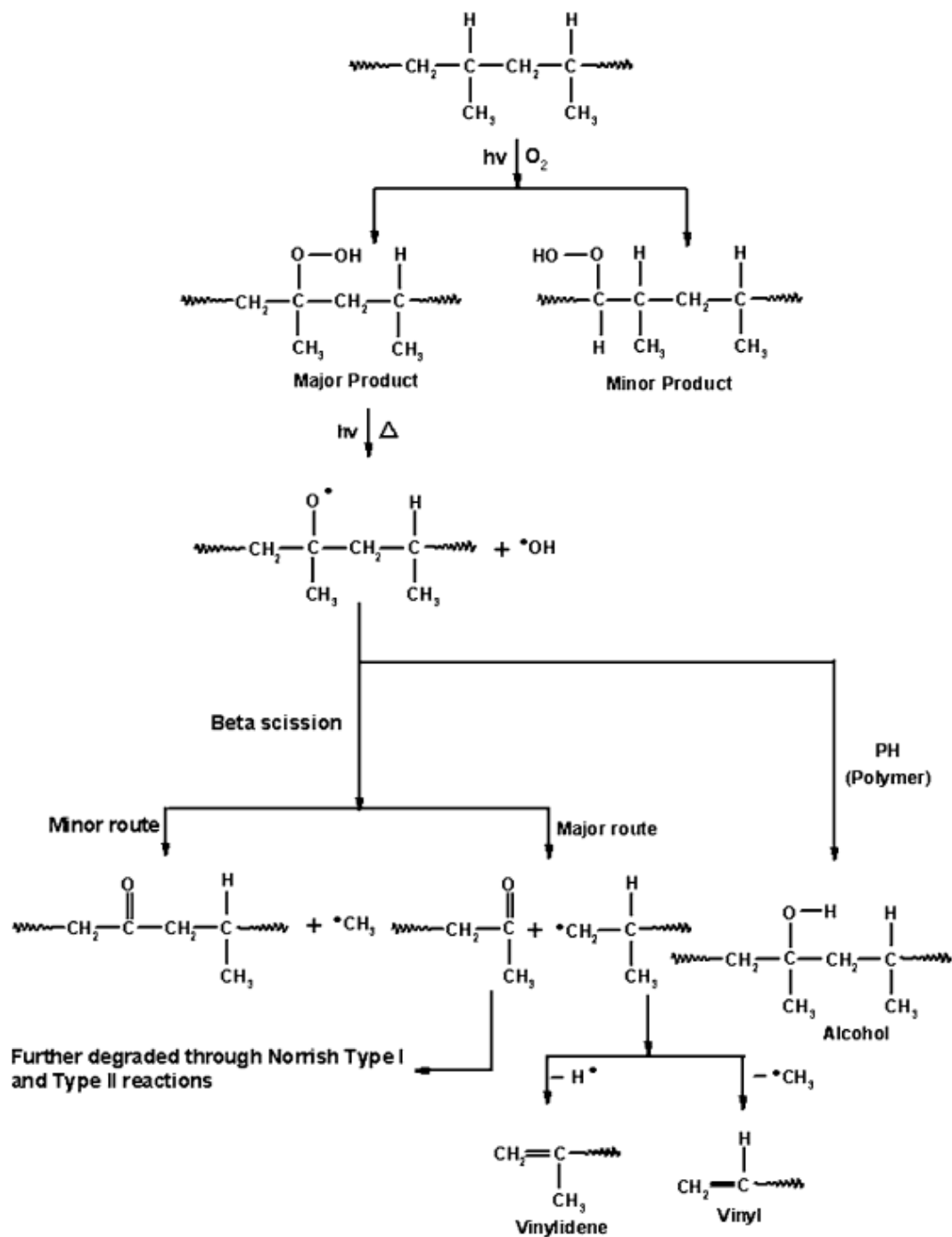


Figure 1.5. Formation of carbonyl compounds in polypropylene during photooxidation .[31].

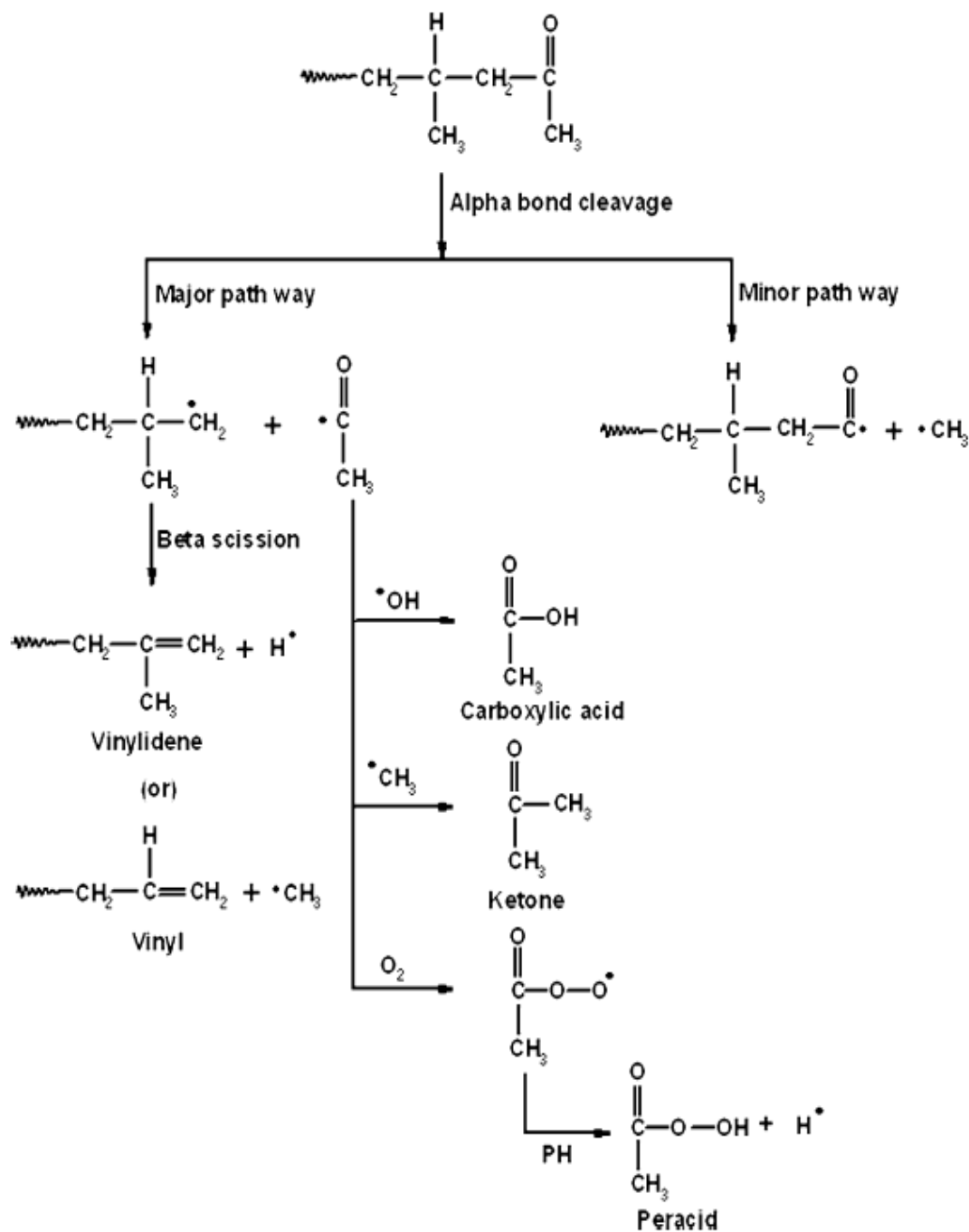


Figure 1.6. Decomposition of carbonyl compounds through Norrish Type I reaction [31].

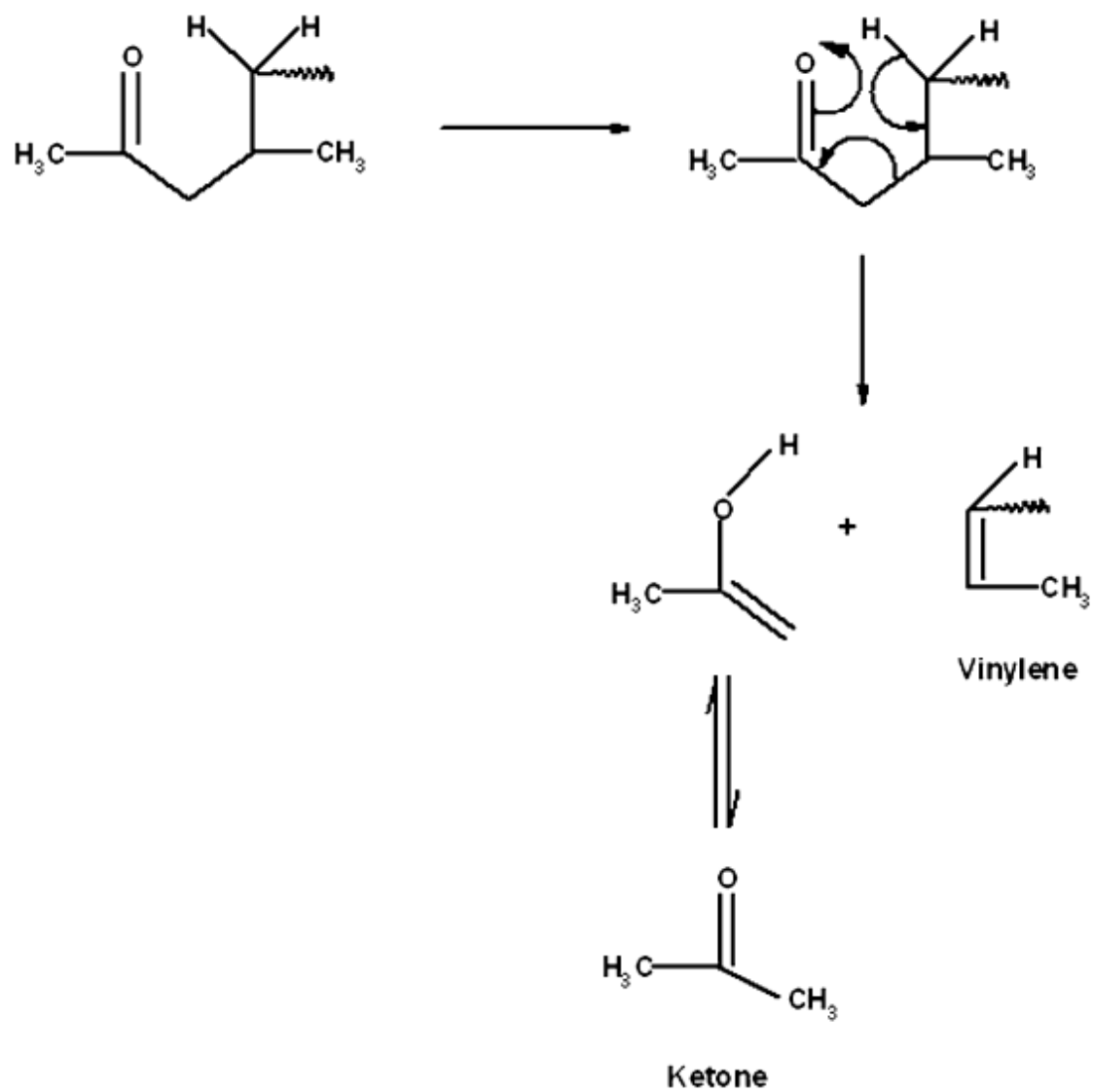


Figure 1.7. Decomposition of carbonyl compounds through Norrish Type II reaction [31].

When polymers are exposed to UV radiation, the activated ketone functionalities can fragment by two different mechanisms, known as Norrish types I and II.

Degradation of polymers with carbonyl functionality in the backbone of the polymer results in chain cleavage by both mechanisms, but when the carbonyl group is in the polymer side chain, only Norrish type II degradation produces main chain scission [32,33]. Also, Norrish I reactions are independent of temperature effects and oxygen concentration at temperature above the T_g of the polymer [34]. The nature of the main oxidation products of PP can be considered as well-established and the mechanism by which oxidation occurs is now fairly well understood [35–37]. They clearly show that the formation of carbonyl products such as ketones, ester and carboxylic acid, hydroxyl products such as hydroperoxide, alcohols and carboxylic acid, and unsaturated compound like vinylidene.

Once the photoactivator reduces the molecular weight down to about 9000, the polymer becomes biodegradable. In the weathering process with some polymers, thermo oxidative degradation is the first step, eventually leading to photodegradation. The primary act in this process is a rupture of bonds of the macromolecules due to heat energy. Free radical sites are produced due to such cleavage of bonds. Subsequently, the radical sites react with the oxygen present in the air to form peroxy radicals. These radicals undergo chain scission to photodegrade by either the Norrish I or Norrish II mechanism discussed previously.

The rate of degradation depends not only on the type and amount of photodegradant present and the type of outdoor exposure, but also on the thickness of the plastic article, amount of pigment, other additives present, and type of polymer used.

Commercial pigments like ZnO, TiO₂, and CdS were examined for their influence on the photodegradation of ethylene–propylene copolymer. The polychromatic irradiation (4290 nm) modified the course of photodegradation. This was evaluated by IR spectroscopy and hydroperoxide determination. These tests showed that the presence of pigments can accelerate or retard the photodegradation depending on their photoactivity.

Clough and Gillen [38] found that radiation dose and temperature act synergistically in promoting degradation.

Cheillini et al. have studied the oxidative degradation of polyethylene under accelerated conditions. Prodegradant additive systems strongly affect the induction of oxidative degradation of the polymer backbone. It was observed that the rate of degradation was directly dependent on temperature of degradation i.e. higher the temperature, higher the degradation of the polyolefin [39].

Overall, polyethylene degradation is a combined photo- and bio-degradation process.

First, either by abiotic oxidation (UV light exposure) or heat treatment, essential abiotic precursors are obtained. Secondly, selected thermophilic microorganisms degrade the low molar mass oxidation products to complete the biodegradation [40].

1.3.2. Biodegradation

The term Biodegradable Plastic can be defined as “a degradable plastic where the degradation results from the action of naturally occurring microorganism such as bacteria, fungi, and algae” (ASTM D 6400-99) [41].

Biodegradable polymers constitute a family of polymers that are designed to be degraded by living organisms such as bacteria and fungi. They offer a possible alternative to traditional nonbiodegradable polymers when recycling is impractical or not economical. This technology is mainly driven by the solid waste problem, decreasing availability of landfills, the litter problem, and pollution of the marine environment by nondegradable plastics [42, 48, 51, 53].

In general, the long chain molecular structure of polymers makes it difficult for the bacteria and fungi to digest the molecular structure. Moreover, the semi-crystalline structure of many plastics means that the entry of water/moisture and enzymes into the polymer matrix is restricted. Also, most synthetic polymers are hydrophobic and hence do not absorb moisture, which is necessary for the existence of most bacteria to cause biodegradation. Attempts to develop new biodegradable polymers have centered mainly synthesis of novel biodegradable backbones, and developing biodegradable polymer composites and blends. [42, 43, 44, 54]

The term “biodegradation” is indicative of the predominance of biological activity in this phenomenon [45]. However, in nature, both biotic and abiotic factors have a role in decomposing organic matter. Several studies about biodegradation of some polymers show that the abiotic degradation precedes microbial assimilation [46-47]. Accordingly, it

is worth elucidating the two major types of degradation that can occur in nature namely abiotic degradation and biotic degradation.

Abiotic degradation is said to occur when polymeric materials are exposed to outdoor conditions (i.e. weather, ageing and burying) can undergo transformations which may be attributed to mechanical, light, thermal, and chemical origins. [45]. Mechanical degradation can take place due to compression, tension and/or shear forces. The causes of these forces are numerous, e.g. a range of constraints during material installation, ageing due to load, air and water turbulences, snow pressure and bird damages. Light degradation involves the usage of UV to initiate chain scission as explained earlier in the Norrish I, II reactions. Thermal degradation of thermoplastic polymers occurs at the melting temperature when the polymer is transformed from solid to liquid (e.g. 159–178 °C for L-PLA depending on its molecular weight, 137–169 °C for P(HB/HV) (poly[hydroxybutyrate-co-hydroxyvalerate]) depending on the percentage of hydroxyvalerate, 175 °C for PHB (poly[hydroxybutyrate]) [47, 51]

On the other hand, biotic degradation involves the degradation of polymers under the action of living organisms present in the environment. Biodegradation is considered to take place throughout three stages: biodeterioration, biofragmentation and assimilation [45]. Of these, biodeterioration is the most significant in synthetic polymers.

Biodeterioration involves the superficial degradation that modifies mechanical, physical and chemical properties of a given material. At least two categories of enzymes are actively involved in biological degradation of polymers: extracellular and intracellular

depolymerases. During degradation, exoenzymes from microorganisms break down complex polymers yielding short chains or smaller molecules, e.g., oligomers, dimers, and monomers, that are smaller enough to pass the semi-permeable outer bacterial membranes, and then to be utilized as carbon and energy sources. This process is called depolymerization and may occur either aerobically or anaerobically as shown in Figure 1.8 below. When the end products are inorganic species, e.g., CO_2 , H_2O , or CH_4 , the degradation is called mineralization. [50, 51, 52]

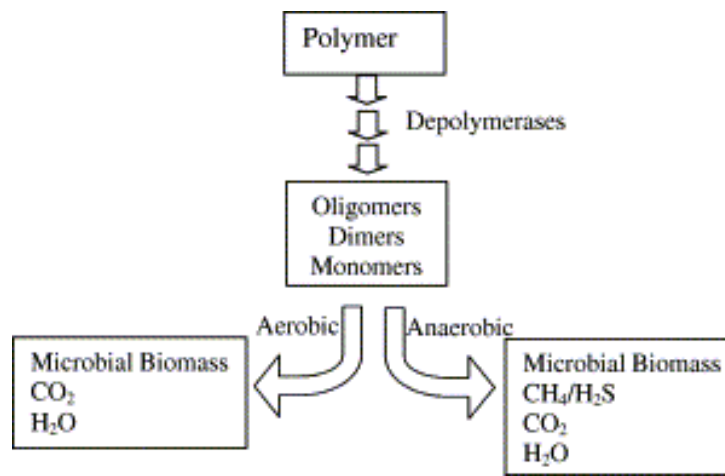


Figure 1.8. Schematic diagram of polymer degradation under aerobic and anaerobic conditions [20].

Oxo-biodegradation process on the other hand, uses two methods to start the biodegradation. These methods are photodegradation (UV) and oxidation. The UV degradation uses UV light to degrade the end product. The oxidation process uses time,

and heat to break down the plastic. Both methods reduce the molecular weight of the plastic and allow it to biodegrade.

Many polymers react with oxygen, especially at high temperatures, and are degraded thereby, the reaction frequently being a chain reaction in which polymer radicals add oxygen to yield peroxy radicals. These in turn attack more polymers, forming a hydroperoxide and regenerating the polymer radical. The oxidation process may be accelerated by further decomposition of the hydroperoxide to generate more free radicals, either photo chemically or by participation of a transition metal ion, which also might be catalyst for the generation of radicals from the polymer.

Although polyolefins are relatively inert, oxidation can occur whenever environmental conditions are favorable. As a consequence, care must be taken to ensure that the stabilization system is adequately formulated. Formation of carbonyl and vinyl groups has been investigated by IR spectroscopic measurements. The most important spectral changes occurred in the carbonyl region, with maximum absorption at 1725 cm^{-1} . The changes in the unsaturation region with maximum absorption at 710 cm^{-1} , corresponding to vinyl groups, are of secondary importance [43].

It is generally accepted that the key intermediates are hydroperoxides, which are always present because of oxidation during preparation or processing, and decompose under the influence of heat, light or transition metal catalysis to produce free radicals. This is illustrated in Figure 1.9 below.

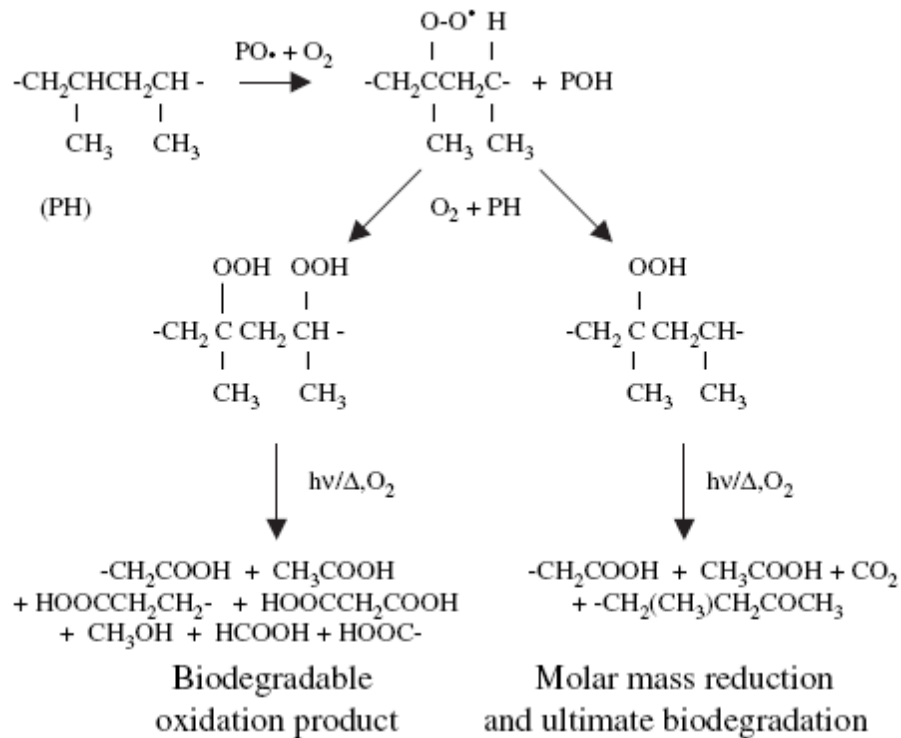


Figure 1.9. Formation and breakdown of hydroperoxides in polypropylene [55].

Once radicals are produced they enter a chain reaction with oxygen and C-H bonds in the polymer, to produce a range of oxidation products. The primary products of this cycle are hydroperoxides, so that oxidation generates its own initiator and has all the characteristics of an auto accelerating chain reaction. The decomposition of hydroperoxides yields alkoxy radicals which are responsible for many secondary products. In particular, β -elimination by alkoxy radicals competes with H-abstraction, and leads to chain scission and formation of a variety of carbonyl products as shown in Figure 1.9. and Figure 1.10. Since linear polymers derive their mechanical properties from the entanglement of their

long chains, limited chain scission causes a rapid change from tough to brittle materials [20].

It is well known that oxidation of polyolefins leads to rapid loss of molar mass and the development of hydrophilic surfaces. Reduction of the molecular weight of PE to values around 40,000, combined with the introduction of oxygen-containing functional groups, leads to biodegradable products.

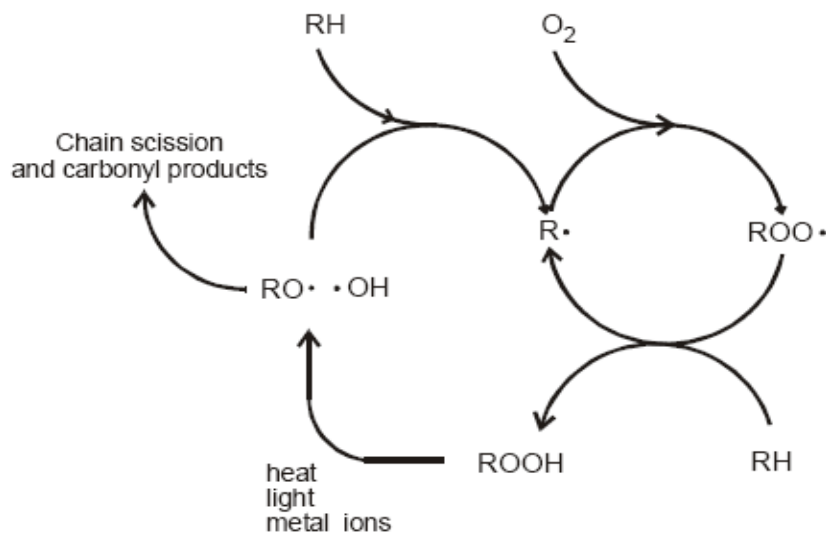


Figure 1.10. Interlocking cycle of reactions leading to oxidation of polymer [20].

In a natural environment microorganisms colonizing a substrate form a biofilm, consisting of bacteria and fungi in a highly hydrated (85-98% water) matrix of extracellular polymers. Both hydrolysis and oxidation of the substrate can be mediated by the biofilm, by release of extracellular enzymes or free radicals. Fungi, in particular, can

spread rapidly by secreting enzymes and free radicals. In addition, insoluble compounds that cannot cross a cell membrane are also susceptible to attack. The mycelial growth habit of fungi also gives a competitive advantage over single cells, especially in the colonization of insoluble substrates. Hyphal penetration provides a mechanical complement to the chemical breakdown, and the high surface-to-cell ratio characteristic of the growing fungi maximizes both mechanical and enzymatic contact with the environment [20, 44, 55].

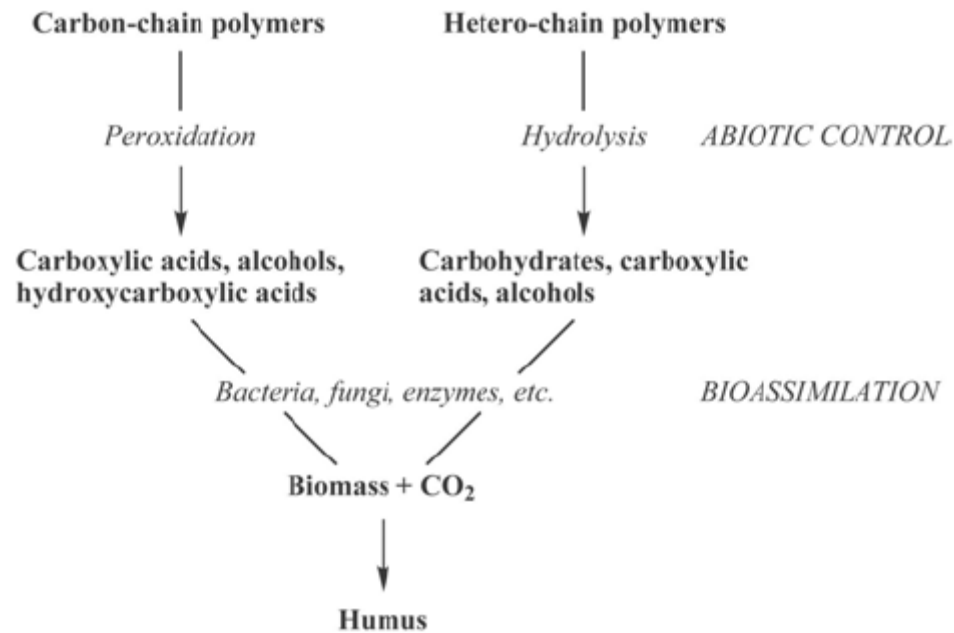


Figure 1.11. Biodegradation routes for oxo and hydro biodegradable polymers [20].

Cell enzymes produced by many bacteria, continue peroxidation by reducing ground-state oxygen to the free radical superoxide. When protonated, these species are converted

to the much more reactive peroxy radicals and hydrogen peroxide, which can be reduced by transition metal ions in the polymer to give the highly reactive hydroxyl radical.

Hydroxyl HO radicals initiate further peroxidation leading to continued biodegradation and ultimate bioassimilation to biomass and CO₂ as long as environmental oxygen and cell nutrients are available. Thus, the bio-assimilation of degraded polyolefins is a synergistic oxo-biodegradation (Figure 1.11). In that sense it is totally analogous to the two-stage, hydro- biodegradation, by which linear polyesters are microbially assimilated [20, 55].

1.4. ADDITIVE TECHNOLOGY FOR DEGRADATION OF POLYPROPYLENE

1.4.1 Additives for plastics

An additive is a substance introduced into a polymer or applied on its surface in order to modify its properties or to enhance its performance. Additives are widely used in the plastics industry to provide polymers with different properties. Melt additives become dispersed in the molten polymer during the compounding process and are bound in the polymer matrix when the polymer cools during fiber quenching. They are generally small organic molecules or minerals introduced at low levels. Polymeric additives introduced at low levels in formulations (less than 10%) can significantly modify or improve properties. In most cases these materials may provide long-term performance like antistatic performance, printability and paint adhesion than lower molecular weight materials or greasy materials. They can be blended with the polymers either during or prior to melt spinning (hence the term ‘Melt additives’) to improve processability, or to impart functionalities like flame retardancy, repellency or hydrophilicity.

[56, 57, 71, 66]

Additives are usually added to PP in the melt stage to provide some useful properties to PP. These include control of static, stiffness, transparency, frictional and adhesion properties etc. Additives may also be added to improve the overall stability of polypropylene during its processing. [71]. The current study aims to study the effect of pro-oxidant additives on the degradability of polypropylene.

1.4.2. Role of additives in biodegradability of polyolefins

The resistance of polyolefins, in general, to biological attack is related to its hydrophobicity, inertness, high molecular weight and its lack of functional groups that can be attacked by enzymatic systems present in microorganisms. All of these properties limit applications of polyolefins in which biodegradation is a desirable attribute.

Major strategies to facilitate polyolefin degradation and subsequent bioassimilation, were focused on the direct incorporation of carbonyl groups within the backbone. Carbonyl groups then serve as reactive centers for the photolytic cleavage of the polymer backbone. Pro-oxidants are used for this purpose.

Additives which act to accelerate hydroperoxide formation and decomposition to radicals are effective pro-oxidants since they accelerate the chain branching reactions. Pro-oxidants, also known as prodegradants, include additives such as polyunsaturated compounds, transition metal ions and metal complexes, such as dithiocarbamates, which rendered polyethylene, and polyolefins in general, susceptible to hydroperoxidation. These functional groups act as initiators of thermal and photooxidation of the hydrocarbon polymer chains. These abiotic degradation processes result in functional macromolecules, which thermally and/or photochemically cleave repeatedly to low molecular weight fragments, especially in the presence of transition metal ions. These low molecular weight oxygenated products include aliphatic carboxylic acids, alcohols, aldehydes and ketones [61, 73, 58, 53].

1.4.3. Mechanism of pro-degradant additives for polyolefins

Pro- oxidants are usually transition metal ions, typically added in form of stearates or other organic ligand complexes, most often stearates of Fe^{3+} , Mn^{2+} or Co^{2+} . Whereas Fe^{3+} complex plays a role in photooxidation process as a source of radicals for reaction initiation, Mn^{2+} or Co^{2+} are necessary for oxidation without the influence of light, when they catalyze decomposition of peroxides associated with chain cleavage. [64, 75, 67, 61]. Under the effect of UV light, the peroxides can be decomposed and chain cleavage occurs after absorption of a photon and without the need for metal ion catalysis (Fig. 1.12).

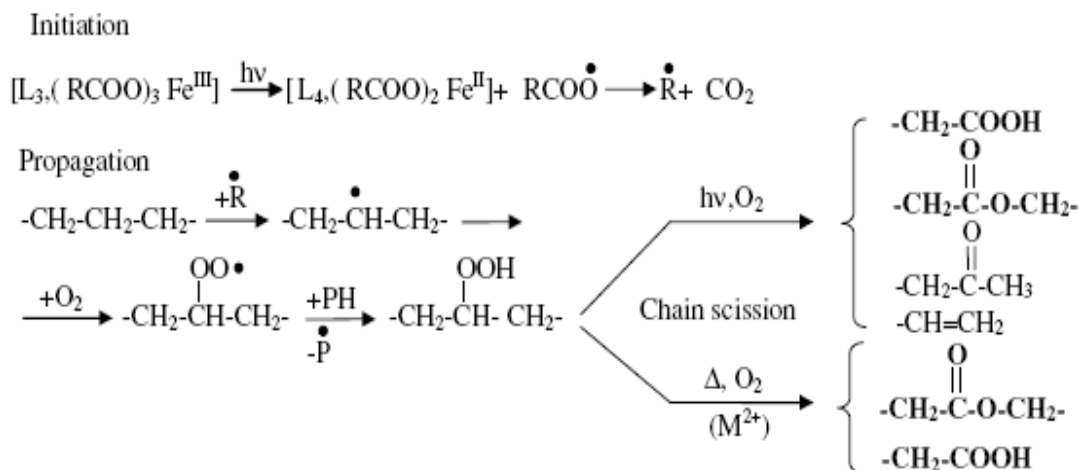


Figure 1.12. Simplified scheme of abiotic degradation of PE with prooxidant content by action of air oxygen, light and/or heat. PH, polymer chain; L, suitable ligand [67].

Because the pro-oxidants and molecular oxygen are present exclusively in amorphous regions of the polymer the oxidation take place there predominantly whereas the crystalline zones remain intact.

Light intensity and temperature have a major role to play in this photo- and thermo-oxidation processes. Chain cleavage results in the formation of carbonyl containing groups but other functionalities like esters, ketones, alcohols and double bonds can also be found. A broad spectrum of low MW compounds is formed as well as mainly, again, various carboxylic acids which can diffuse to the environment and eventually be extracted to aqueous media.

Another matter of concern is that polyolefins that are industrially manufactured are inherently stable since they contain anti-oxidants which are added in small amounts to provide good shelf life to the final end product. These anti-oxidants inhibit the oxidation of polyolefins and prevent their degradation. Hence it has been shown that by using a balanced combination both antioxidant and prooxidant additives, PE film can be prepared that maintains all its mechanical and processing properties during the life cycle of the product and then loses mechanical properties relatively quickly and undergoes further degradation under the influence of the pro-oxidant used. [59]

Degradation studies of additive containing films can be carried out by subjecting them to accelerated degradation under conditions of high light intensity and elevated temperatures. Degradation is exhibited by a dramatic shift of the whole MW distribution and a decrease of the weight-average MW from several hundreds of thousands to several

thousands. Macroscopically oxidation manifests itself as loss of mechanical properties and film fragmentation, which is caused by the disruption of connecting chains between semicrystalline regions. An increase of hydrophilicity and wettability of the film surface may also be observed. Apparently, the resulting material seems to be much more suitable for microbial attack than the initial PE film. Since it has been proved that this pre-oxidation is an important step in the degradation of polyolefin films, it is usually recommended that biodegradation studies be conducted for these films after exposing samples to light radiation and/or increased temperature [65, 62, 60, 78].

1.4.4. Commercially available pro-oxidant additives

There are several additives which can be obtained commercially to manufacture biodegradable polyolefin films as listed below:

1.4.4.1. TDPA [Totally Degradable Plastic Additives TDPA™]

TDPA™ is a product of EPI Environmental Products Inc. which has been developed to control the lifetime of conventional polyethylene, polypropylene and polystyrene resins. [20].

These additives work on the principle of oxidative biodegradation i.e. Oxo biodegradation. Oxo-biodegradable additives require the presence of oxygen and some form of activation energy like light (UV) or heat for the initial oxidative degradation of the polymer back-bone [55]. Different oxo-biodegradable additives, using different transition elements/metals will have variable sensitivity to light and/or heat. For instance,

it has been demonstrated that iron is significantly activated on UV exposure. [68, 55, 72, 76, 77]

The steps of oxo-biodegradation are 1) *oxidative degradation* (radical chain scission and oxygenation [adding hydroxyl and carboxyl groups]) [55,76], followed by 2) *biodegradation* by microorganisms (fungi, bacteria, etc.) [64, 67, 74, 61, 40]. These mechanisms have been studied in detail and it has been proved that these additives do make conventional plastic (PE and PP) biodegrade according to ASTM D5338 [11,61]

The exact chemical composition of these additives is not known due to copyright.

However, the patents filed by EPI Environmental Products Inc. refer to degradable/compostable additive packages for adding to polyolefin resins used in the manufacture of packaging materials to make the specific packaging product degradable/compostable. It is claimed that these additive packages are a combination of a metal carboxylate and an aliphatic poly hydroxy-carboxyl acid. [70]

The metal carboxylates may include cobalt, cerium and iron stearate etc. The aliphatic poly hydroxy-carboxyl acid has been defined as an aliphatic acid having either more than one hydroxy (-OH) or more than one carboxyl (-COOH) group in the organic acid. These may include carboxylic acids like glyoxylic acid, citric acid, or malic acid. These additives are available in pellet form which may also include additional oxidizing agents like calcium oxide [70].

Chiellini et al. has demonstrated the biodegradability of thermally oxidized, fragmented low density polyethylenes. Thermally degradable low-density polyethylene samples containing TDPA TM pro-oxidant additives from EPI Inc. were submitted to an investigation aimed at evaluating their ultimate biodegradation (e.g. mineralization) in soil and mature compost incubation media. High mineralization level accompanied by structural changes in the samples indicated that LDPE-TDPA formulations are effective in promoting the oxidation and subsequent biodegradation of polyethylene in soil environments. [61]

Mohee et al. has studied the biodegradability of TDPA and Mater-bi containing plastics under aerobic and anaerobic conditions. It was observed that TDPA containing samples did not show a weight loss under aerobic conditions of biodegradability whereas the biodegradability tests under anaerobic conditions indicated that the samples had biodegraded at rates significantly different from each other. This may indicate that that the TDPA containing samples may need to be pre treated with UV and then composted in order to biodegrade the samples completely. [63]

PE bags containing TDPA additive were studied by Raninger, using the municipal composting plant of Vienna Neustadt. It was observed that the TDPA modified PE bags underwent biodegradation during the composting operation. The resulting compost product, which contained particulate and partially biodegraded plastics, was premium quality material and passed all the usual ecotoxicity tests. These included seed

germination, plant growth and organisms' survival (daphnia, earthworms) tests carried out in accordance with DIN V 54900-3, ON S 2200 and ON S 2300 national standards. [69]

1.4.4.2. ECM Additives

ECM Biofilms, manufactures different grades of ECM MasterBatch Pellets™ which are added during manufacturing as masterbatch pellets. The company's technology is a process that enables the microorganisms in the environment to metabolize the molecular structure of plastic films into a humus form that can be further metabolized and eventually rendered as minerals that are beneficial to the environment and conducive to plant growth.

The additive is a proprietary formulation that is mixed with carrier resins to make a masterbatch pellet. The masterbatch pellets can then be easily added to plastic resins using a plastic product manufacturer's existing equipment. This biodegradation process can take place aerobically and anaerobically. It is claimed that the degradation can take place with or without the presence of light. It is claimed that these factors allow for biodegradation even in landfill conditions that are normally not conducive to plastic degradation and keep the plastic degradation from occurring when not desired [79].

1.5. COMPOSTING

Composting is an accelerated biooxidation of organic matter passing through a thermophilic stage (45 to 65°C) where microorganisms (mainly bacteria, fungi and actinomycetes) liberate heat, carbon dioxide and water. The heterogeneous organic material is transformed into a homogeneous and stabilized humus like product through turning or aeration.[82] .There are various systems of composting that includes Windrow Composting, Aerated Static Pile composting, vermicomposting etc.

Windrow composting (Figure 1.13) consists of placing the mixture of raw materials in long narrow piles which are turned mechanically on a regular basis to aerate the piles. The turning operation mixes the composting materials and enhances passive aeration. Typically, the wind-rows are from 90 cm high for dense materials such as manures to 360 cm high for light, voluminous materials such as leaves. They vary in width from 300 to 600 cm. The size, shape and spacing of the wind-rows are influenced by the equipment used for turning. [86]



Figure 1.13. Windrow composting field [86].

However, usually within an hour after turning, oxygen levels in a pile often drop drastically, and microbial activity is correspondingly reduced. For this reason, the pile must be turned frequently. This in fact is a major drawback of the windrow system, leading to technical and economic problems. Moreover, pile size is another important constraint, because piles higher than three meters become difficult to aerate. [86, 89,87, 84]

In forced aerated static piles (Figure 1.14), a blower provides air to the composting mass. The main feature that distinguishes the “aerated static pile” (ASP) from the windrow system of composting, is the mode of aeration. While periodic turning is used as a means of achieving aeration in the windrow, aeration is provided by forcing air through the static pile either by sucking “negative pressure mode” or blowing “positive pressure mode” [83,88]

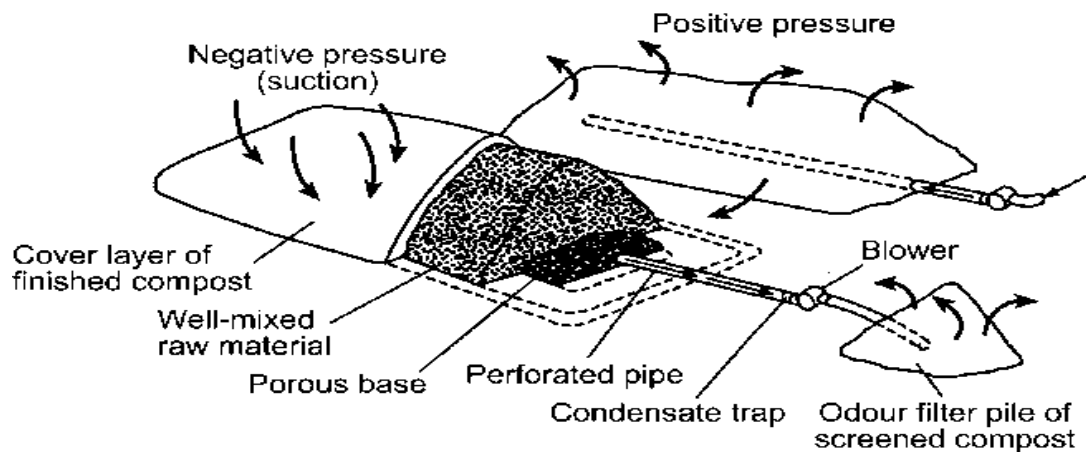


Figure 1.14. Aerated static pile layout [86].

In continuous vertical reactors, the materials usually are loaded through the top of the reactor and discharged from its bottom. Oxygenation is provided by forcing air up from the bottom through the composting mass. These reactors are typically of high capacity (as much as 2,000 cubic meters) and may be as high as nine meters. The height of the reactor is extremely critical and masses higher than three meters lead to serious problems in ventilation.

On the other hand, in horizontal reactors, the materials are arranged along the length of the unit and the depth never exceeds two or three meters. The principal advantage of these systems is the ability to control the process, resulting in a shorter duration of the thermophilic stage than in the open systems. Because oxygen is supplied either by turning or by aeration, the composting mass can be uniformly oxygenated and the temperature can be readily controlled. [82, 86]

Vermicomposting is also a biooxidation and stabilization process of organic material that, in contrast to composting, involves the joint action of earthworms (Figure 1.15) and microorganisms and does not involve a thermophilic stage [82]. The process of turning, fragmentation and aeration is carried out by earthworms. Certain species of earthworms can consume organic residuals very rapidly and fragment them into much finer particles by passing them through a grinding gizzard, an organ that all earthworms possess. The earthworms derive their nourishment from the microorganisms that grow upon the organic materials. [82, 89]



Figure 1.15. Vermicomposting with redworms [80].

At the same time, they promote further microbial activity in the residuals so that the fecal material, or "casts" that they produce, is much more fragmented and microbiologically active than what the earthworms consume. During this process, the important plant nutrients in the organic material -- particularly nitrogen, phosphorus, potassium and calcium -- are released and converted through microbial action into forms that are much more soluble and available to plants than those in the parent compounds [82, 85].

Anastasi et al have studied the diversity and functions of the mycoflora of both a green compost (made solely thermophilically from plant debris) and a vermicompost. These studies of the role of fungal biodiversity in vermicomposting conditions indicate that

lignin and plastic polymer degradation were significantly higher in the vermicompost. as compared to a green compost.[81]

In the present study, the effects of vermicomposting and soil burial on additive containing polypropylene and control 100 % polypropylene nonwovens have been studied. Though degradation studies of polyolefin films have been carried out earlier, no such studies have been carried out for additive containing polyolefin fibers and nonwovens. This study thus aims to study the degradability of pro-degradant additive containing polypropylene fibers and nonwovens using xenon exposure, vermicomposting and soil burial as the method of degradation.

SECTION 2- EXPERIMENTAL

2.1. MATERIALS

In the present work, polypropylene of melt flow rate 36 (g/10 min), from Exxon Mobil (PP3155) was used to make melt spun filaments and nonwovens. TDPATM additives were procured from EPI Inc. Four ECM MasterBatch PelletsTM additives namely ECM 0702, ECM 0701, ECM 0404, ECM 0204 were procured from ECM Biofilms Inc. The additives were in the form of pellets. For the sake of abbreviation, TDPATM and ECM MasterBatch PelletsTM will be referred to as TDPA and ECM respectively.

2.2. RHEOLOGY STUDIES

The Thermo Haake Minilab Equipment (Minimelter) with the twin-screw extruders was used to examine the polymer response to different temperatures and shear rates under a nitrogen purged environment. This machine is generally used to study polymer degradation process as a function of process temperature and residence time or for compounding studies for new polymer blends. The construction of this equipment comprises an extrusion chamber connected to a backflow channel where polymer viscosity is measured on continual basis as the polymer circulates between the extrusion and backflow chambers. The melting viscosities of PP and PP with 1 and 5 % of TDPA and ECM additives polymers were measured. A sample size of 5 grams was used. The polymer with additive was subjected to the action of torque of rotating twin screws at a temperature of 250 C for time duration of 15 minutes at a frequency of 150 min⁻¹. A plot of resultant torque and viscosity versus time was obtained.

2.3. POLYPROPYLENE FILAMENTS WITH TDPA AND ECM ADDITIVES

2.3.1. Melt spinning of PP filaments with TDPA and ECM additives

The PP fibers with 1 % and 2 % TDPA and ECM additives were melt spun on the Hill's Bicomponent Machine to produce undrawn filaments. Table 2 shows the spinning parameters that were used:

Table 2. Process parameters for melt spinning of filaments.

Spinneret	288 hole (round)
Samples	Control PP PP with 1, 2 % TDPA additives PP with 1, 2 % four ECM additives
Spin Block	255 °C
Extruder Zone Temperature	
Zone 1	220 °C
Zone 2	230 °C
Zone 3	240 °C
Feed Roll Speed	440 m/min
Winder	445 m/min
Extruder Pressure	400 psi
Pack Pressure	390 psi
Denier	659.2
Spin Finish	Lurol PP-L425

2.3.2. Xenon exposure of PP filaments with TDPA and ECM Additives

The filaments were exposed to UV radiation in an Atlas Hi 3 Sun Weatherometer which uses water cooled xenon lamp operating at 6500 watts and calibrated at 340 nm. (shown in Figure 2.1). This apparatus is used to study the effect of accelerated degradation under conditions of elevated temperature and humidity.

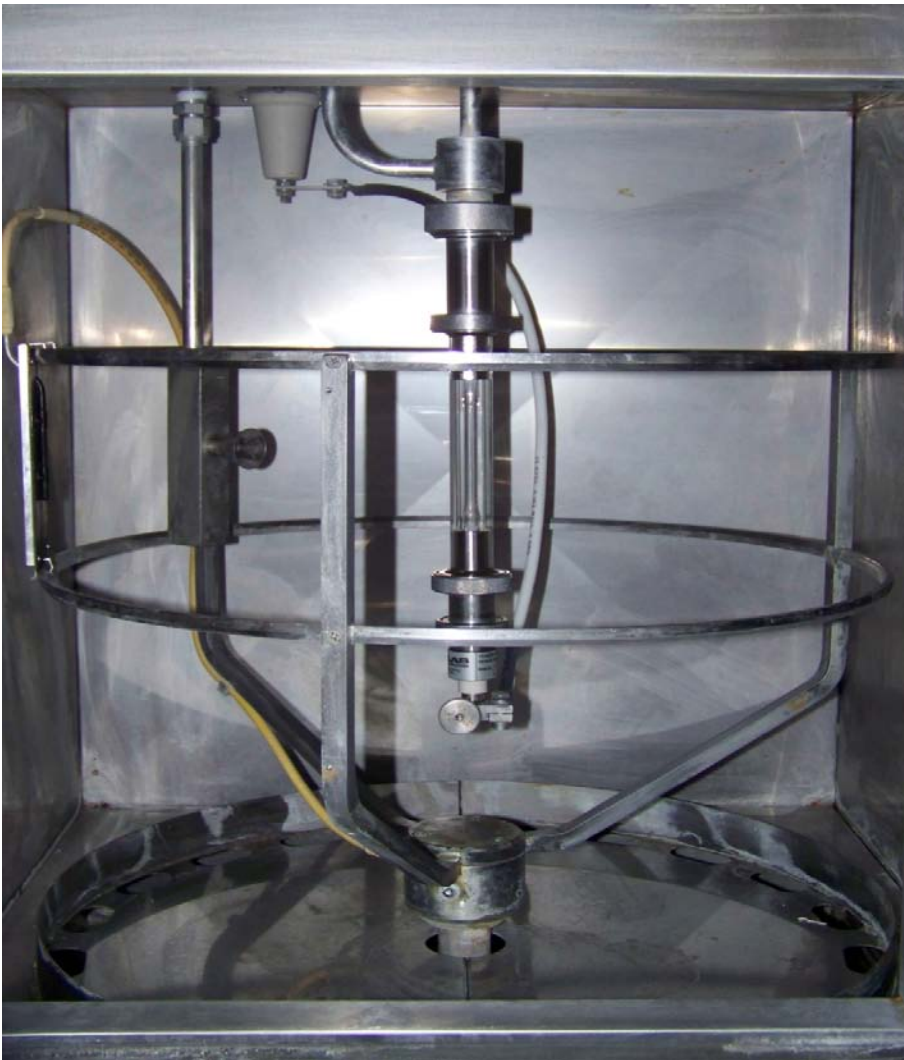


Figure 2.1. Atlas Hi 3 Sun Weatherometer.

Figure 2.2 shows the winding of filaments on the sample holder specially designed for exposing filaments to xenon lamp action in the Weatherometer. The holder was made of aluminum and was provided with aluminum hooks to enable wrapping of filaments on the plate. This ensured that an adequate length of filament is exposed to UV simultaneously.

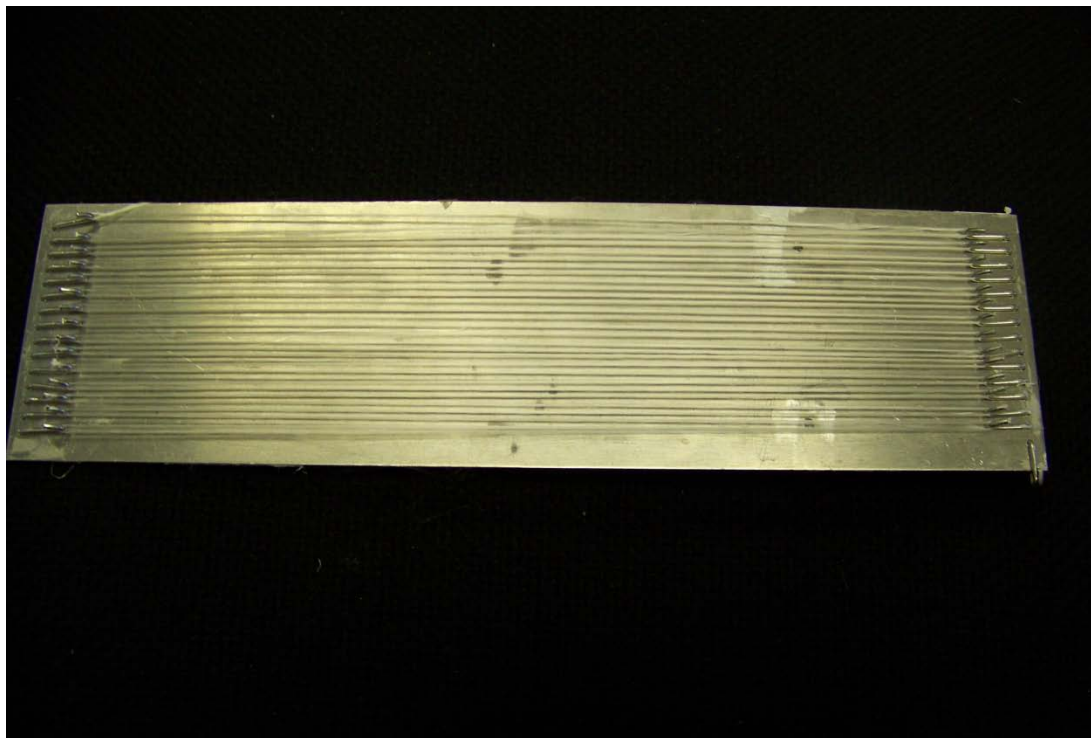


Figure 2.2. PP Filaments wound on the Aluminum Sample Holder.

The filaments were subjected to accelerated weathering (simulating Miami conditions) at elevated temperatures of 42 °C, relative humidity of 79 % for 80 and 180 hours. Subsequently, the samples were subjected to tensile testing, SEM Imaging and FTIR analysis.

2.3.3. Tensile studies of PP filaments with TDPA and ECM additives

The elongation at break, modulus and tenacity are very important physical characteristics of a filament. Elongation is the ratio of the extension of a material to the length of the material prior to stretching, expressed as a percent. The Instron tensile strength tester was used to test the tensile properties of these filaments as per "Standard Test Method for Tensile Properties of Yarns by the Single-Strand Method", ASTM D2256 using a sample size of 10. All samples were conditioned to the standard testing conditions i.e. 70 °F and 65 % RH prior to testing. A gauge length of 5 inch, with a break sensitivity of 75% and a cross head speed of 300 mm/min was used for this method. To avoid slippage of the filaments at the jaws, the filaments were gripped with masking tape at their ends.

2.3.4. FTIR spectroscopy of PP filaments with TDPA and ECM additives

Attenuated total reflectance (ATR) spectra were collected on a Nicolet 560 FTIR spectrometer, with a germanium crystal , equipped with an Advantage microscope and using liquid nitrogen cooled Mercury Cadmium Telluride (MCT) detector. At least 32 scans were obtained to achieve an adequate signal to noise ratio. The spectral resolution was 2 cm⁻¹. Since studies previously conducted indicate the formation of carbonyl group containing compounds on degradation, carbonyl index and hydroxyl index evaluation was done from the spectra obtained. [31]

2.3.5. Scanning Electron Microscopy of PP filaments with TDPA and ECM additives

Morphology of the filaments after xenon exposure was studied with an Hitachi S-3200N Scanning Electron Microscope (SEM). The surface of the cut filament was coated with a layer of gold before viewing.

2.4. POLYPROPYLENE SPUNBOND NONWOVENS WITH ADDITIVES

2.4.1. PP Spun bond nonwoven manufacturing

Spunbond homo-component and I/S samples were produced at NCRC Pilot facilities located at the North Carolina State University. The schematic diagram of the spunbonding machine used is depicted in Figure 1.2. The spinning parameters are enlisted in Table 3.

Table 3. Process parameters for manufacture of spunbond nonwovens.

Spin Pack	1162 hole
Samples	100 % PP Control PP with 2 % TDPA additives PP with 2 % ECM additives (3)
Throughput	0.6 ghm (grams/hole/minute)
Spin Head Temperature	466 °F
Type	Sheath/ Core
Calender Pressure	750 psi
GSM (grams / sq. meter)	30

2.4.2. Basis weight calculation of PP spunbond nonwovens with TDPA and ECM additives

One of the most important properties of a fabric is its basis weight. Many properties including strength, thickness, porosity, tearing strength, and others are influenced by changes in the basis weight of the fabric. The basis weight of the spunbond samples was defined using “Standard Test Method for Mass Unit Area of Nonwoven Fabrics” (ASTM D6242-98). All samples were conditioned at $65 \pm 2\%$ relative humidity and $21 \pm 1^\circ\text{C}$ temperature prior to testing. Ten specimens with the length and width of 4 inches (10.16 cm) were cut from each of the fabrics and weighed with a calibrated balance to 0.1%.

The mass per unit area was calculated for each specimen to the nearest 0.1 g/cm^2 using the following equation

$$M = S/A$$

Where: M is mass per unit area, (g/cm^2); S is mass of specimen, (g); A is area of specimen (cm^2). The average values of the fabric basis weight and standard deviation for each sample were reported.

2.4.3. Thickness and Flexural Rigidity of PP Spunbond Nonwovens with TDPA and ECM additives

The thickness of the fabrics was determined as the distance between the upper and the lower surfaces of the material, measured under a specified pressure, using “Standard Test Method for Thickness of Nonwoven Fabrics” (ASTM D5729-97). A pressure foot was $25.40 \pm 0.02 \text{ mm}$, and the applied force was 3.3 psi. 10 readings were obtained from each

of the samples. Flexural Rigidity was assessed as per Standard Test Method for Stiffness of Nonwoven Fabrics Using the Cantilever Test, ASTM D5732.

2.4.4. Xenon exposure of PP spunbond nonwovens with TDPA and ECM additives

The filaments were exposed to UV radiation in an Atlas Hi 3 Sun Weatherometer which uses water cooled xenon lamp operating at 6500 watts and calibrated at 340 nm. (shown in Figure 2.3). The nonwovens were mounted in a holder as shown in Figure 2.3

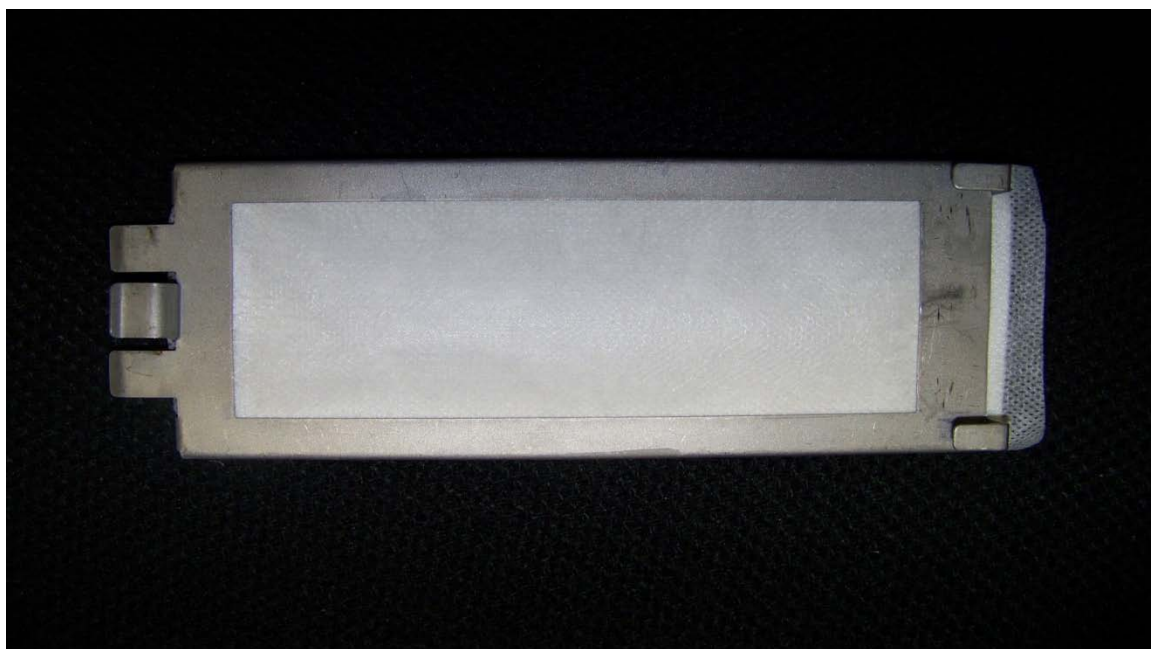


Figure 2.3. Sample holder for xenon exposure of nonwovens.

Miami conditions of 42 °C, relative humidity of 79 % were used for a time period of 80 and 180 hours. Subsequently, the samples were subjected to tensile testing, SEM imaging and FTIR analysis.

2.4.5. Vermicomposting of PP spunbond nonwovens with TDPA and ECM additives

The vermicomposting of Nonwovens was done at the Vermicomposting Facilities at NCSU. The study was conducted in a 10 ft length x 5 ft width composting bin as shown in Figure 2.44. The compost comprised composting worms, hog manure and water. An average temperature of 60-77 °F was maintained. The nonwoven samples were suspended by polypropylene strings from a wooden plank as shown in Figure 2.4. Samples were drawn out on a weekly basis and subjected to a vermicomposting time period of 4 weeks . The samples were then studied for weight change, tensile, FTIR and SEM analyses.



Figure 2.4. Vermicomposting bin with polypropylene samples hanging from the strings.

2.4.6. Soil burial of PP spunbond nonwovens with TDPA and ECM additives

In order to study the effect of soil burial on polypropylene, both control and additive containing nonwovens were buried in a pit on campus at NCSU, at a depth of 5 inches. Samples were of 2 inch length x 2 inch breadth dimensions. Samples were drawn out on a

weekly basis for a period of 4 weeks. The next set of samples was drawn out after a 3 month and 6 month soil burial. The drawn out samples were cleaned in water at room temperature and oven dried at 50 °C. The samples were then studied for weight change, tensile, FTIR and SEM analyses.

2.4.7. Weight change analysis after vermicomposting and soil burial

The samples were studied for a change in weight after vermicomposting and soil burial by weight measurement on an electronic digital balance. For higher accuracy, the samples were weighed in grams rounded off to the 4th decimal place.

2.4.8. Tensile studies of PP spunbond nonwovens with TDPA and ECM additives

The Instron tensile strength tester was used to test the tensile properties of nonwovens after degradation studies (xenon exposure, vermicomposting, soil burial) as per ASTM D5034 - 09 “ Standard Test Method for Breaking Strength and Elongation of Textile Fabrics (Grab Test)”. All samples were conditioned to the standard testing conditions i.e. 70° F and 65 % RH prior to testing. A gauge length of 1 inch, with a break sensitivity of 50% and a cross head speed of 12 in/min was used for this method. Sample size of 10 with sample dimensions of 1”x1” was used. To avoid slippage of the filaments at the jaws, the filaments were gripped with masking tape at their ends.

2.4.9. FTIR and SEM of PP spunbond nonwovens with TDPA and ECM additives

FTIR and SEM studies for nonwovens were done similar to those for the filaments.

SECTION 3- RESULTS AND DISCUSSIONS

The results and discussions will be discussed in two parts as mentioned below

3.1) Characterization of PP filaments with TDPA and ECM additives

3.2) Characterization of PP Nonwovens with additives

3.1. CHARACTERIZATION OF PP FILAMENTS WITH TDPA AND ECM ADDITIVES

3.1.1. Study of Melt Rheology to analyze the suitability of spinning filaments with additives

Before proceeding with the melt spinning of the PP fibers with additives, it was necessary to study the effect of these additives on the melt rheology, so that the possibility of spinning additive containing filaments could be analyzed. One of the advantages of the Minilab is that it is capable of continuously monitoring the apparent viscosity of the polymer melt during processing. The significance of viscosity in melt processing of polymers is that it gives an indication of degradation reactions which lead to a change in molecular weight, which is strongly correlated with viscosity.

In order to arrive at the optimum concentration of additive to be used, trials were carried out to study the melt behavior of the polymer with 1 and 5 % of additives. In general, it was observed that with time, for a fixed shearing rate and temperature, viscosity initially increased and showed a plateau. The control PP without any additives recorded a

viscosity of approximately 20 Pa·s, after 15 minutes of shearing. This is shown in Figure 3.1

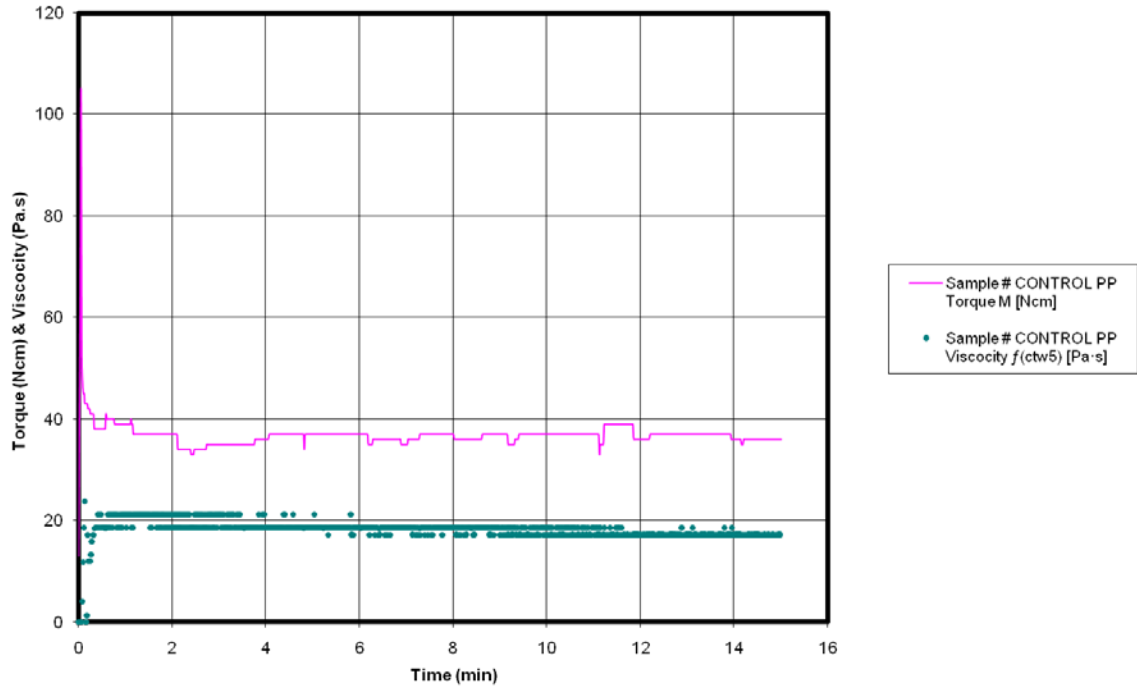


Figure 3.1. Torque and viscosity measurements for control polypropylene.

As compared to this value, all samples containing 1 % concentration of additive, showed a viscosity value almost similar to control Polypropylene. However 5 % additive containing samples showed an erratic trend with an increase in viscosity in some cases (TDPA) and a slight decrease in viscosity in some cases (ECM 0702). This may indicate that the presence of additive in higher concentration affects the melt behavior of the polymer due to either shear thickening or shear thinning which may vary according to the nature of the additive used.

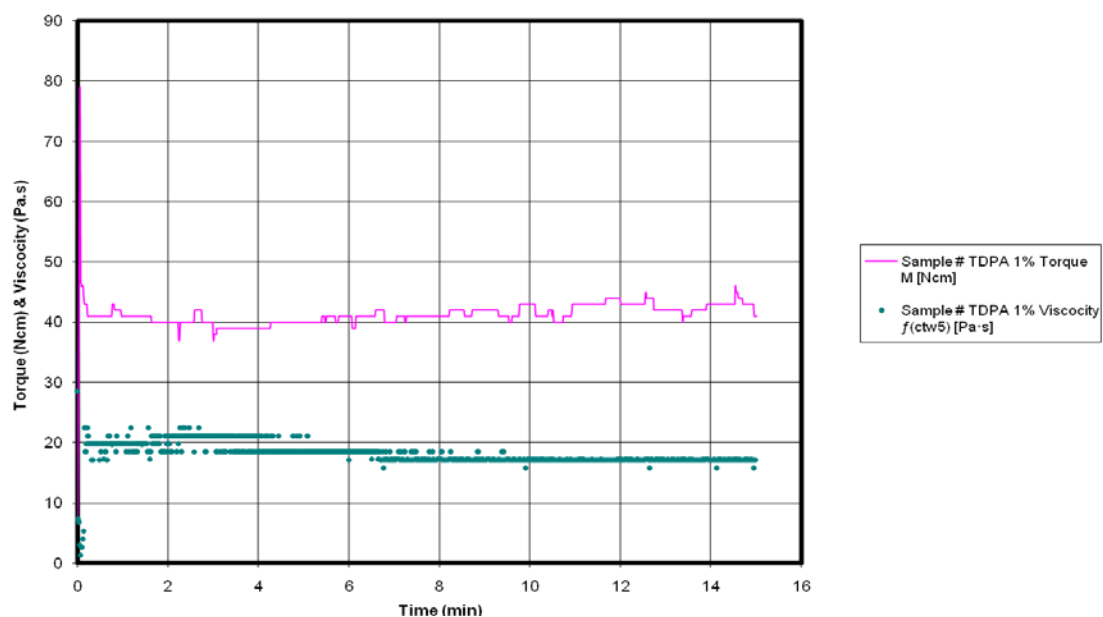


Figure 3.2. Torque and viscosity measurements for polypropylene with 1 % TDPA.

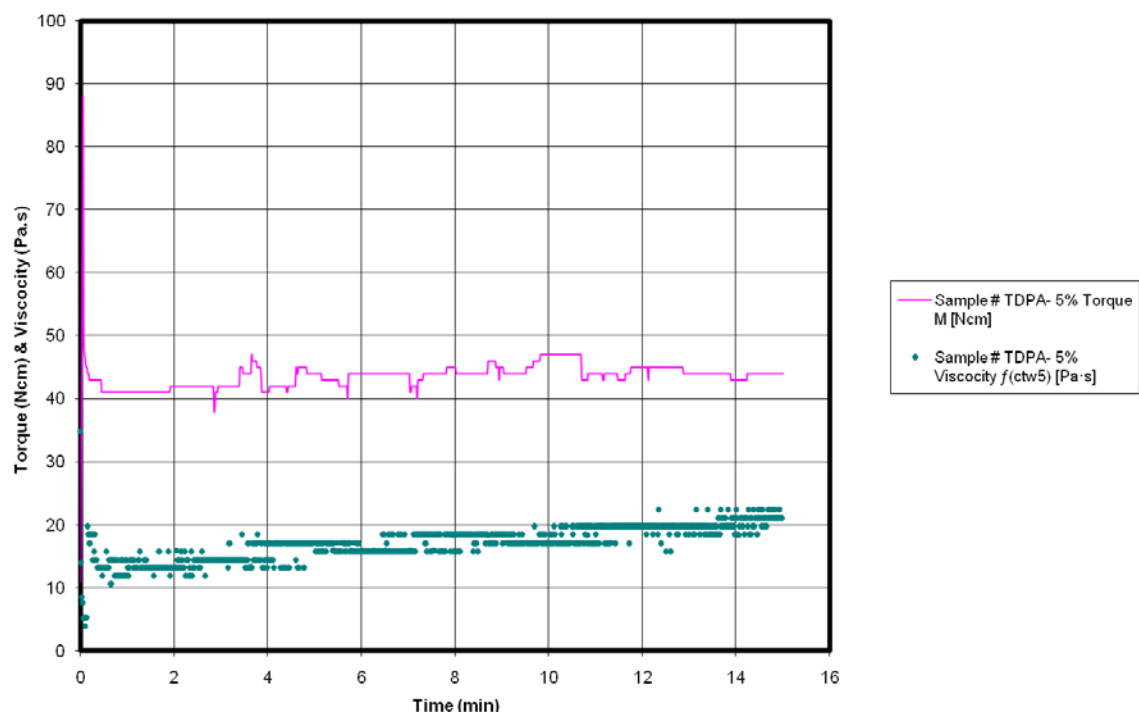


Figure 3.3. Torque and viscosity measurements for polypropylene with 5 % TDPA.

The Mixing torque is yet an important indicator of the processing characteristics of polymer blend especially when internal mixing is employed. In this particular rheology study conducted, the mixing torque of each system was recorded against the time of mixing. Typical torque vs. time curves of the PP–additive systems are shown in Figure 3.2 and 3.3

In general, the recorded torque can be divided into two portions namely the peak torque and stabilization torque. The peak torque corresponds to the peak at the first few minutes of the experiment that appears on the torque–time curves whereas the stabilization torque is the torque that appears after approximately 5 min of mixing. The first sharp peak torque approximately at the first minute usually corresponds to the first addition of solid material which in this case is PP pellets with additives. The instant increase in torque can be attributed to the high shear force to rotate the rotor in the presence of PP pellets just before they melt. As the PP melts, the viscosity of PP decreases under high temperature and shear and consequently decreases the torque of mixing. This is clearly observed in the case of control PP (Figure 3.1). After the initial peak followed by the drop, the torque almost remains constant throughout the experiment time.

In case of PP-additive systems, a trend similar to this was observed. In case of 1 % as well as 5 % TDPA additive usage (Figure 3.2 and Figure 3.3), the initial torque recorded does not vary significantly with an increase in the additive percentage. However in the case of PP- ECM 0702 system, the initial torque recorded in case of 1 % concentration of additive is very high compared to the torque recorded in case of 5 % additive

concentration. This may indicate that the presence of this particular additive in the system at higher values serves as lubricant which is also indicated by the lower viscosity values observed after 14 minutes.

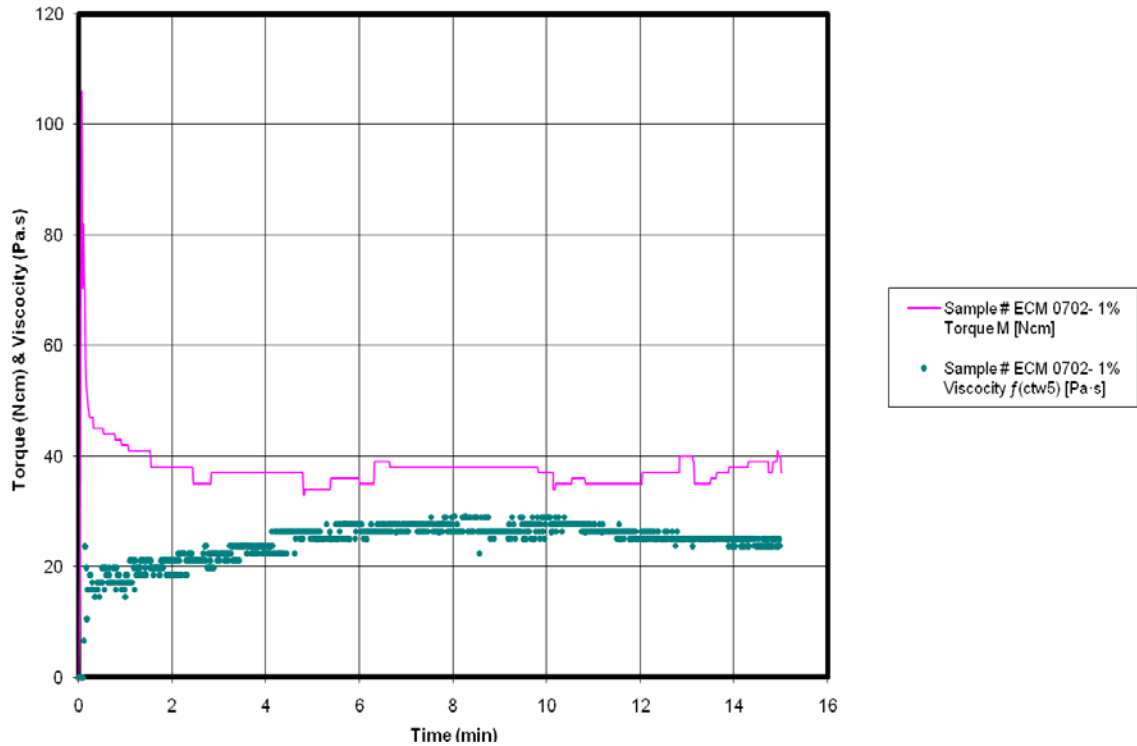


Figure 3.4. Torque and viscosity measurements for polypropylene with 1 % ECM 0702 additive.

From the above graphs, it is clear that that the melt viscosity remains consistent with time and temperature. In fact, an increase in viscosity in cases with higher (5%) concentration of additive has been observed. The objective of using the Minilab was to determine if the the additives resulted in the deterioration of melt properties or adverse shear thinning.

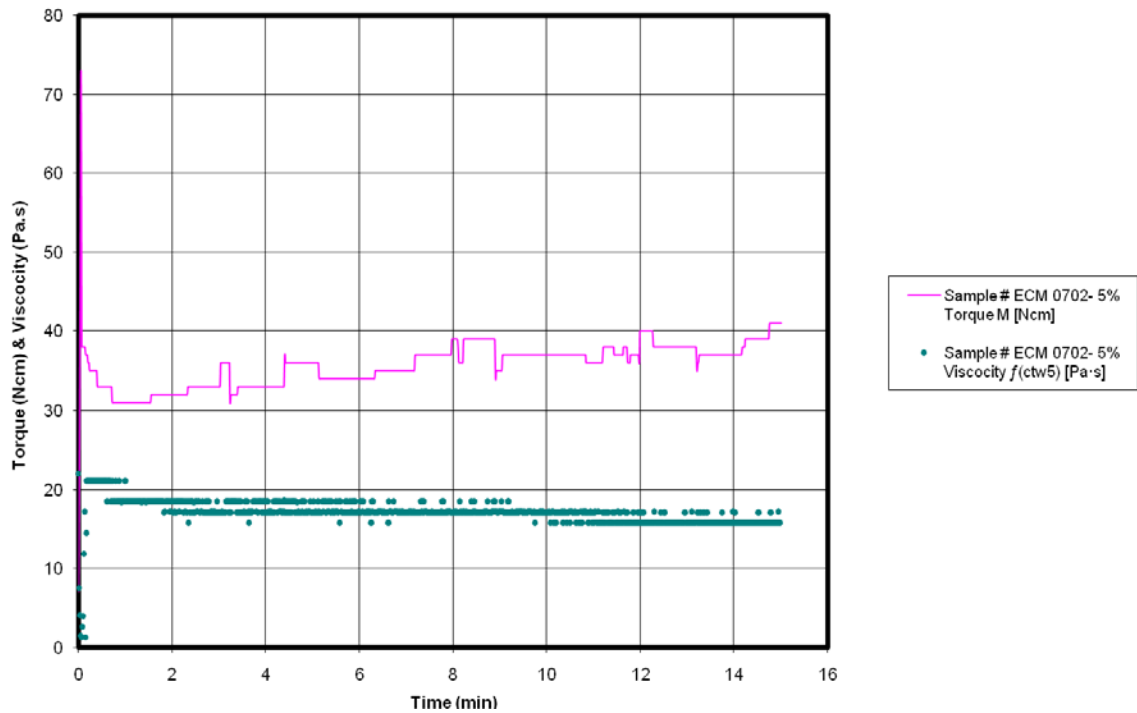


Figure 3.5. Torque and viscosity measurements for polypropylene with 5 % ECM 0702 additive.

As seen from above, when used in smaller concentrations (1%), the additives do not affect the shear viscosity to a large extent. This shows that PP filaments can be spun with 1 % concentration of additives without complications. However, usage of 5 % of additives in the melt altered melt behavior to some extent, causing shear thinning as well as shear thickening in some cases. This was accompanied by a large value of torque which may cause wear and tear of the extruder screws. Hence, to ensure that the effect of additive on melt properties was minimal, it was decided to spin filaments with 1 % and 2 % concentration of additives.

3.1.2. Melt spinning of filaments with TDPA and ECM additives

The orientation of filaments can be altered by varying the spinning speeds used in the melt spinning machine. Higher spinning speeds results in the formation of more oriented filaments. Since these PP multifilament yarns made as a precursor to PP spunbond nonwovens show low degree of orientation, undrawn filaments of approximately 659 denier were made at low spinning speeds of 440 m/min. Melt spinning of undrawn polypropylene filaments with 1% and 2 % additives was carried out with a spin block temperature of 255°C. An increase in spin pack pressure was expected in additive containing samples due to shear thickening of the polymer melt due to presence of additives. However, it was possible to produce all additive containing samples at the same pack pressure as that of 100 % PP filaments. (390 psi). However, spinning of filaments with 1% as well as 2 % of additive ECM 0404 resulted in formation of broken filaments with high unevenness. A repeat trial yielded the same results. Hence these filaments were excluded from further analysis. To summarize, the following samples were tested:

- 1) Control PP (100 % PP)
- 2) PP + TDPA (1%, 2 %)
- 3) PP + ECM 0701 (1%, 2%)
- 4) PP + ECM 0702 (1%, 2%)
- 5) PP + ECM 0204 (1%, 2%)

3.1.3. Tensile testing of filaments with TDPA and ECM additives after xenon exposure

The xenon arc lamp consists of a burner tube and a light filter system to provide a spectral distribution that approximates natural sunlight exposure conditions. The apparatus has a built in re-circulating system that recirculates deionized water through the lamp. The water cools the xenon burner and filters the long wavelength infrared [100]. Thus it is the spectral energy produced by the lamp using xenon gas as the inert gas, which is used to treat the samples with UV radiation. However, for the convenience of the discussion, an abbreviation of “*xenon exposure* of samples” has been used instead of “*xenon arc lamp exposure*” of samples.

A water cooled xenon arc lamp is one of the most popular indoor exposure tests because it exhibits spectral energy distribution similar to that of sunlight found at the surface of the earth. The amount of heat received by the sample can be controlled by the usage of black panel thermometers [100]. As compared to other lamp sources like carbon arc lamps, and UV lamps, the xenon arc lamp has the closest spectral distribution to natural sunlight. This is especially true at the UV spectrum from 290-400nm and particularly below 350 nm where most of the degradation of thermoplastics takes place [100]. Hence, the machine was calibrated at a specific wavelength of 340 nm which is equivalent to 1 % of the energy of the entire UV range.

Tensile testing of these filaments after xenon exposure was carried out. Previous studies on degradation of photo-sensitized polyolefin films indicate that degradation is shown

initially by changes in the tensile properties of the films, specifically, a decrease in the elongation at break of exposed films. [91]

Hence a study of changes in elongation, tenacity and modulus after xenon exposure was conducted. In general, it was observed that as the xenon exposure time increased, the elongation at peak load for these filaments decreased. This reduction in elongation is more pronounced in additive containing samples (Figure 3.6).

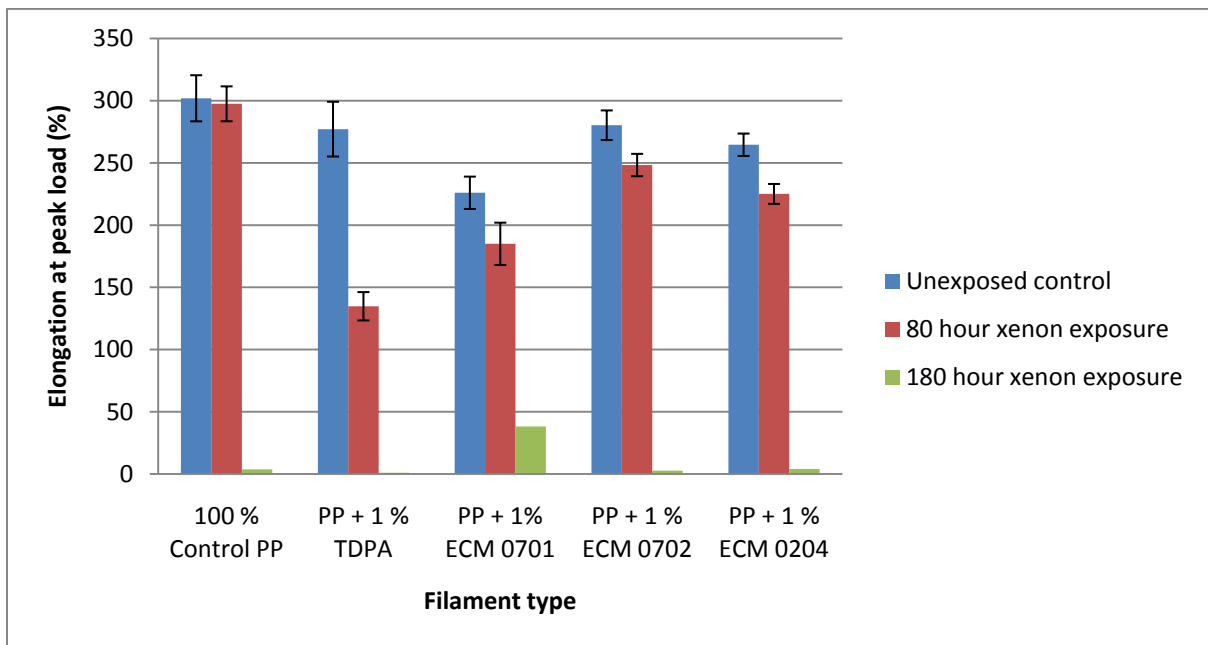


Figure 3.6. Elongation at peak load of PP filaments with 1 % TDPA and ECM additives after 0, 80, 180 hours xenon exposure.

Figure 3.6 shows the elongation at peak load recorded in samples containing 1 % of TDPA and ECM additives. In the case of 100 % PP filaments, the loss of elongation observed after 80 hour of xenon arc exposure was not significant. This is indicated by the overlapping of the respective error bars. Increasing the exposure time to 180 hours

resulted in a 98% reduction in elongation in 100 % PP filaments. This shows that only after increased duration of xenon arc lamp exposure does 100 % PP filament degrade significantly.

However as compared to control 100% PP, 1 % TDPA additive containing filaments showed significant reduction in elongation (almost 52 %) after just 80 hours of xenon arc lamp exposure. 180 hours of xenon arc lamp exposure resulted in almost a 100 % reduction in elongation in 1 % TDPA containing samples.

After 80 hours of xenon arc lamp exposure, all samples containing 1 % ECM additive recorded a drop in the elongation at peak load values. ECM 0701 containing samples showed an 18 % decrease whereas ECM 0204 and 0702 showed a 15 % and 11 % decrease in elongation at peak load values respectively. Though this drop is significant compared to the control 100 % PP filament, this decrease is not as significant as in TDPA additive containing samples. It is only after prolonged exposure that ECM additive containing samples were able to show an effective decrease in elongation at peak. After 180 hours of xenon arc lamp exposure, ECM 0702 , ECM 0701 and ECM 0204 additives showed a 99%, 83 % and 98 % reduction in elongation at peak load respectively. This shows that ECM additives, when used at 1 % concentration are effective in reducing the elongation at peak load of PP only under conditions of higher UV exposure.

Nevertheless, it was observed that both TDPA as well ECM additive containing samples showed a larger drop in elongation values as compared to 100 % PP filaments when exposed to UV. This clearly indicates that both additives, TDPA as well as ECM effectively help to accelerate degradation of PP when used even at 1 % concentration.

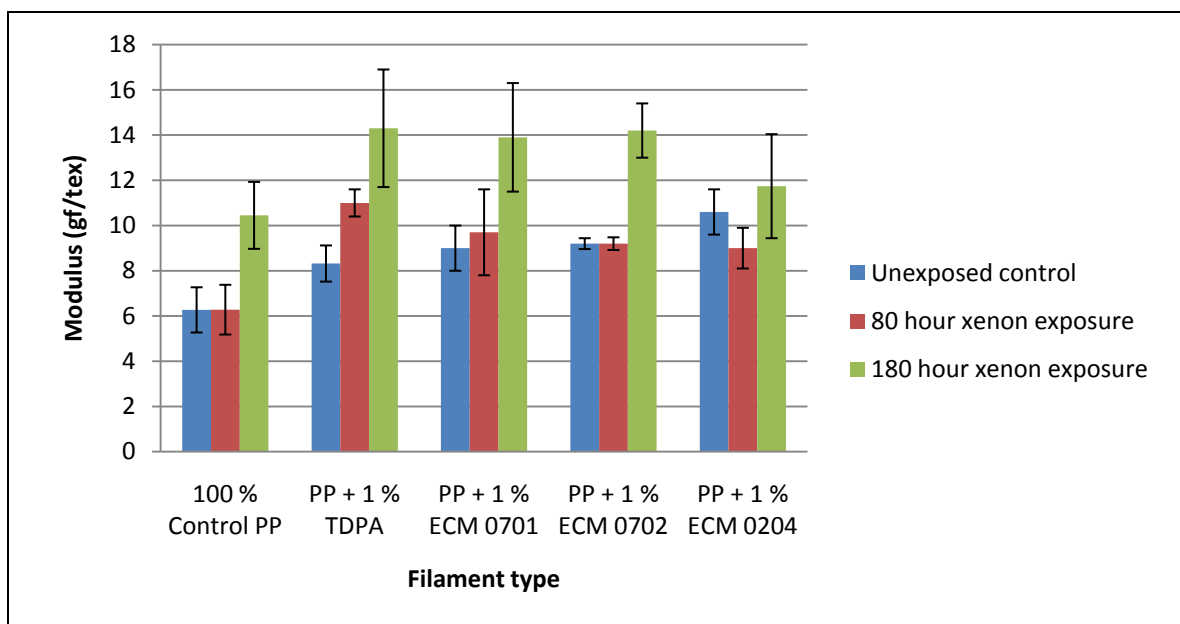


Figure 3.7. Modulus of PP filaments with 1 % TDPA and ECM additives after 0, 80, 180 hours xenon exposure.

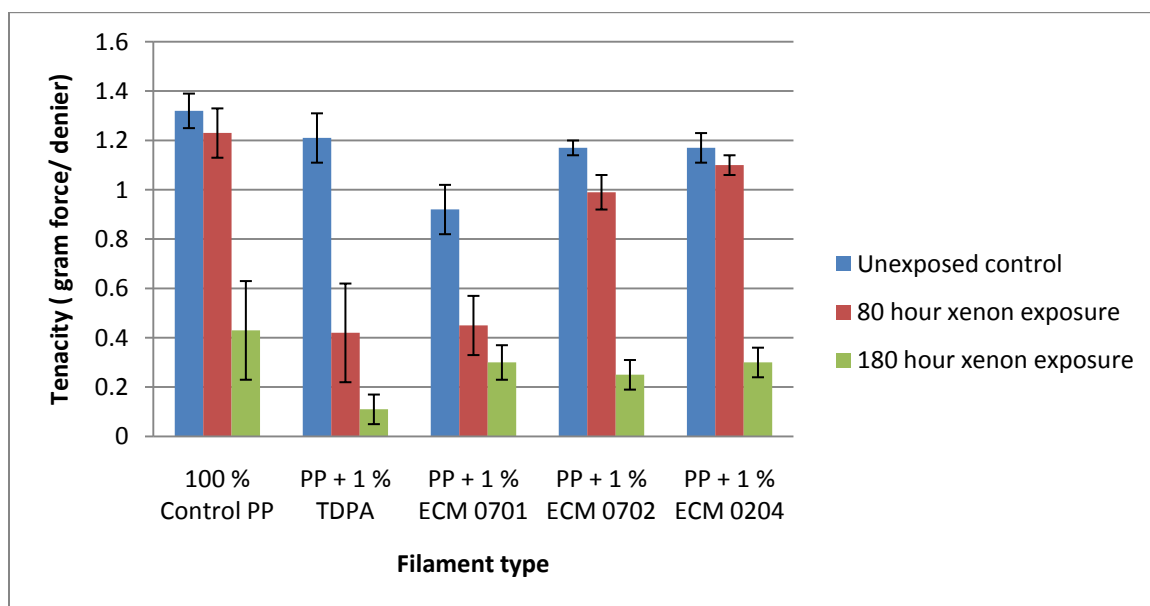
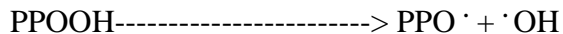


Figure 3.8. Tenacity of PP filaments with 1 % TDPA and ECM additives after 0, 80, 180 hour xenon exposure

Figure 3.7 shows the modulus values recorded in samples containing 1 % of ECM and TDPA additives. It can be said that increasing the duration of UV exposure results in an increase in the modulus of the sample thereby indicating the occurrence of embrittlement of the sample. The increase in modulus is more pronounced in additive containing samples as compared to the control 100 % PP filaments, more so in the case of TDPA additive containing samples. As shown in Figure 3.8, a reduction in average tenacity of the samples was also observed with increasing duration of xenon arc lamp exposure. However, in case of 100 % PP, a significant reduction in tenacity was observed only after 180 hours of xenon arc lamp exposure. As compared to this, TDPA additive containing samples showed significant reduction in tenacity after just 80 hours of xenon exposure. ECM additive containing samples also show a significant loss in tenacity after 80 hour xenon exposure. However, the decrease observed in ECM additive containing samples is not as phenomenal as compared to that in TDPA additive containing samples.

It is known that the strength in these fibers arises from the extensive entanglement of polymer segments in the amorphous zones between crystallites. Only the amorphous zones of polypropylene are readily penetrable by oxygen. Hence it can be inferred that most of the observed photooxidation damage is concentrated in this region. The photooxidation of polypropylene results in the formation of both hydroperoxides as well as peroxides. The photocleavage of hydroperoxides results in the formation of macroalkoxy radical hydroperoxide photocleavage by the process



This macroalkoxy radical may cause the beta scission of the backbone chain. It is this backbone chain cleavage that can be attributed to the catastrophic drop in tensile properties observed in these filaments. [14, 28, 29]

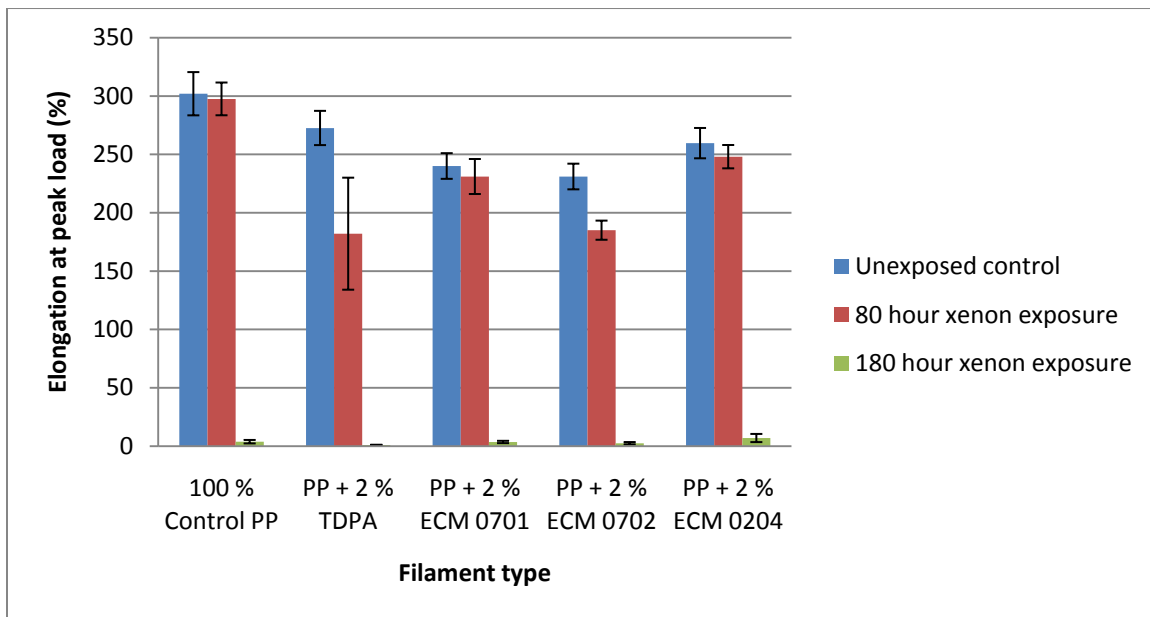


Figure 3.9. Elongation at peak load of PP filaments with 2 % TDPA and ECM additives after 0, 80, 180 hours xenon exposure.

There are two factors that play a major role in reduction of mechanical properties. Firstly, the duration of xenon exposure and secondly the percentage of pro-degradant additive used. While in all cases it was observed that increasing the xenon exposure timing reduced the tensile properties drastically, the increase in additive concentration does not necessarily cause a reduction in tensile properties.

Figure 3.9 shows the values for elongation at peak load values for samples containing 2 % of ECM and TDPA additives. In case of TDPA containing samples, after a 180 hour xenon exposure, almost equal elongation values are obtained for both 1 and 2 % of additive concentration. Hence the addition of more additive does not seem to have altered the degradation rate to a large extent. It is observed that the duration of xenon exposure is more important and more degradation can be obtained by increasing the duration of xenon exposure even if low concentration of TDPA additive is used.

Similar trend has been in ECM 0702 containing samples. It was observed that increasing the exposure time to 180 hours reduced the elongation by more than 97%. However, increasing the additive content did decrease the elongation at peak load as significantly as varying the exposure timing. This may perhaps indicate that the degradation mechanism in these additives is more dependent on the period of xenon exposure than the concentration of additives used.

In the case of ECM 0701 containing sample, however, it can be seen that both the percentage of additive as well as exposure time have a major role to play in degradation. It is seen that significant decrease in tensile properties is seen only if higher additive concentration is coupled with increasing xenon exposure.

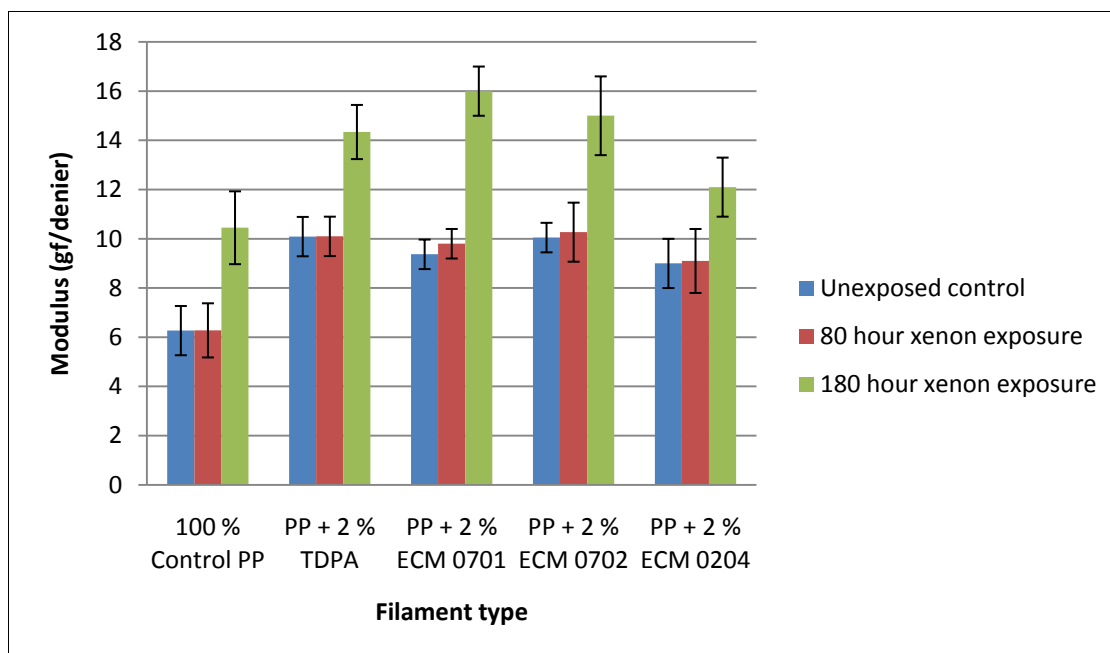


Figure 3.10. Modulus of PP filaments with 2 % TDPA and ECM additives after 0, 80, 180 hours xenon exposure.

It was observed that the exposed samples do show slightly high coefficient of variation (C.V.). This may be due to the differential degree of fibers being exposed to UV owing to their spatial arrangement on the plates. Also, it was observed that the nature of degradation in additive containing exposed samples were such that some samples were too weak to even be mounted on the tensile testing machine. This could also have contributed to the high variation observed in additive containing samples.

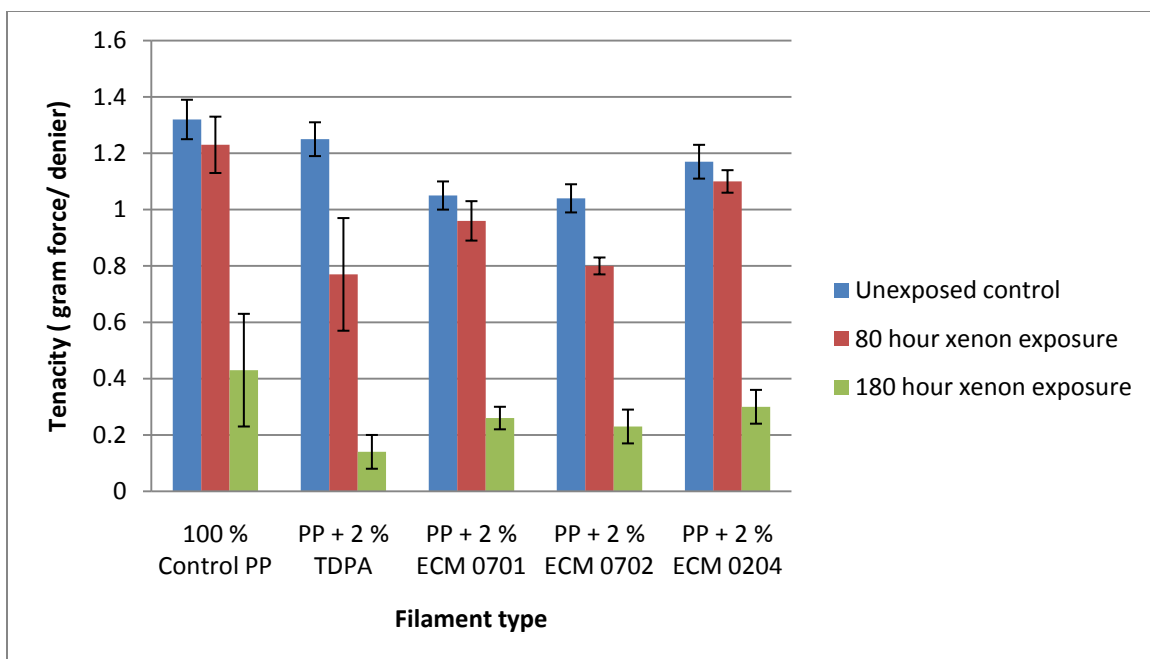


Figure 3.11. Tenacity of PP filaments with 2 % TDPA and ECM additives after 0, 80, 180 hour xenon exposure

It was also observed that all samples show an increase in modulus on UV exposure, which is indicative of samples getting brittle (Figure 3.10). Almost a 100% increase in modulus was observed in additive containing samples. Also, the samples showed a reduction in tenacity on UV exposure, which is more pronounced in additive containing samples especially after 180 hour. xenon exposure (Figure 3.11). Thus, it can be inferred that from a ductile nature with large elongation, the polymer changed to a brittle behaviour, with very low elongation at break. The tensile strength is drastically reduced, a common aspect in degraded PP where chain scission is the most frequent degradation pathway.

To summarize, TDPA additives are very effective in aiding degradation of PP in presence of xenon exposure, even when used at smaller percentage (1%). ECM additives are effective in degrading PP only when used at higher percentages (2%). This shows that TDPA is much more effective in degrading PP than ECM additives. However, duration of UV exposure is also a major factor and 180 hour of xenon arc exposure can lead to phenomenal decrease in the tensile strength of the samples containing TDPA and ECM additives. It can be clearly observed that additives do accelerate the degradation of PP, TDPA being a better pro-degradant than ECM. Yet another reason for the decay in mechanical properties may have been the formation of surface cracks caused by surface densification. To further study the nature of cracks, an SEM analysis was carried out. The chemistry of degradation was studied using the FTIR.

3.1 .4. FTIR of Polypropylene Filaments with TDPA and ECM Additives after xenon exposure

The degradation of polyolefins in the presence of UV is indicated by the Norrish I, II mechanisms. As indicated in these reactions the peroxidation of polyolefin results in the formation of carbonyl group containing products like carboxylic acids, esters, aldehydes, etc. These show up in the FTIR spectrum in the form of peaks in the carbonyl and hydroxyl region. The main products of degradation, carbonyls and hydroperoxides, are easily observed respectively in the wavelength ranges 1700-1800 and 3300-3600 cm^{-1} as shown in a typical spectrum in Fig. 3.12.

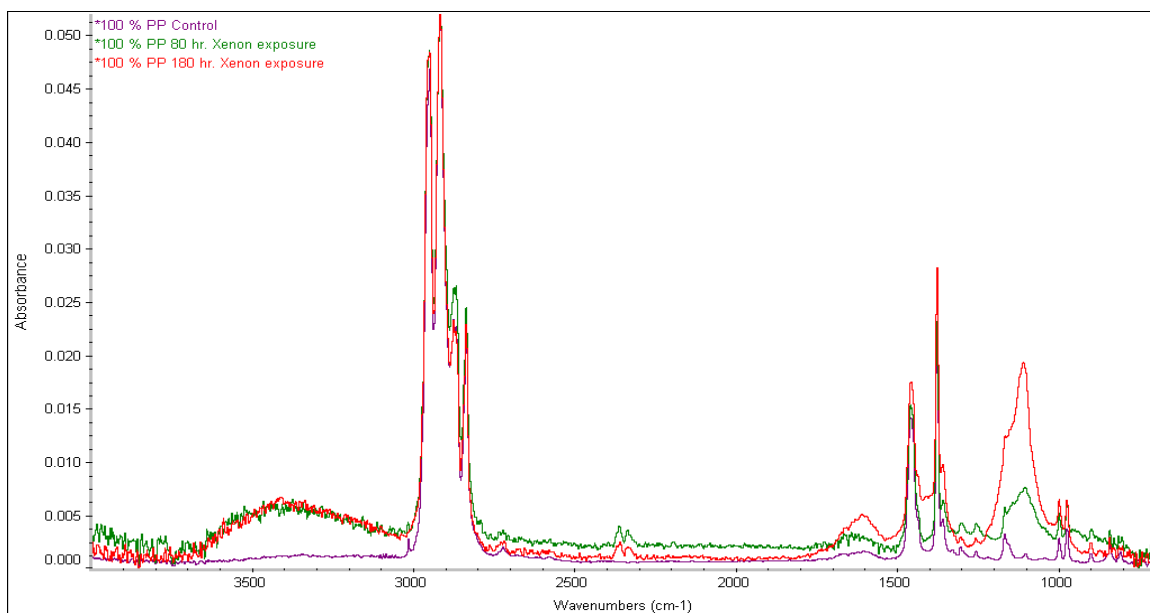


Figure 3.12. FTIR spectrum for PP filaments at samples at 0, 80 and 180 hours of xenon exposure.

These peaks tend to be fairly broad because they are the result of absorption by different products of degradation. Quantitative determinations of the carbonyl index were taken as the relative areas under the carbonyl peak and a reference peak. It was necessary to ensure that the reference peak chosen should not be affected by degradation and should be fairly isolated from other absorptions. Chain scission releases previously entangled chain segments and allows them to crystallize. If enough material of this kind becomes available to crystallize, it is more likely that these segments will attach to the growth faces of pre-existing crystals nearby. This will increase crystallinity and is a form of secondary crystallization often known as ‘chemi-crystallization’. Several peaks were found in the literature to be used as a reference for polypropylene like 840, 1166, 1455

and 2720 cm^{-1} . The first two are also sensitive to the crystallinity of PP and are not suitable because of chemi-crystallization effects. The peak centered at 1455 cm^{-1} is overlapped with several others, which makes the determination more difficult and, besides, is also related to the orientation of PP. The peak at 2720 cm^{-1} was chosen as the most appropriate and although small when compared with the others, reproducible determinations were achieved [31, 92]. This absorption is associated with CH bending and CH, stretching. Accordingly, carbonyl index and hydroxyl index was computed to verify the presence of these compounds. Carbonyl index was calculated as a ratio of absorbance at 1610 cm^{-1} (corresponding to the carbonyl peak) to the absorbance at 2920 cm^{-1} (corresponding to the C-H peak). Hydroxyl index was calculated as a ratio of absorbance at 3340 cm^{-1} (corresponding to the carbonyl peak) to the absorbance at 2920 cm^{-1} .

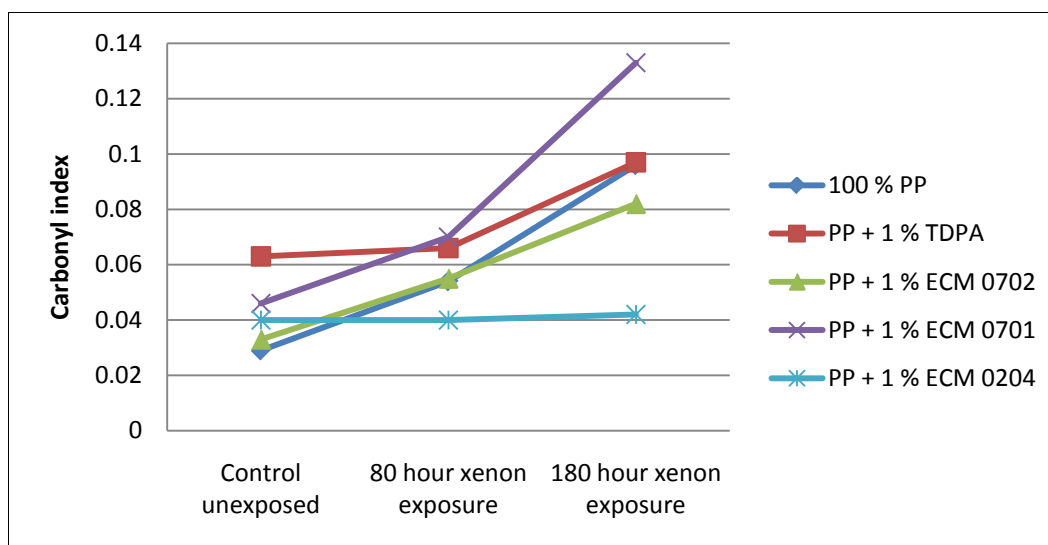


Figure 3.13. Carbonyl index for 1 % TDPA and ECM additive containing filaments for 0, 80 and 180 hours of xenon exposure.

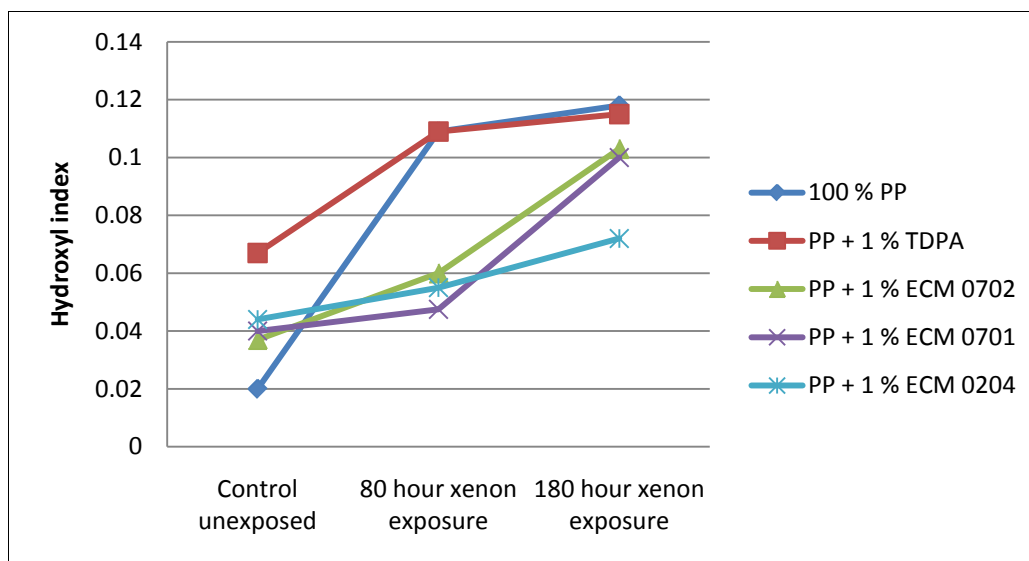


Figure 3.14. Hydroxyl index for 1 % TDPA and ECM additive containing filaments for 0, 80 and 180 hours of xenon exposure.

Figure 3.12 shows the spectra obtained for filaments before and after 80 and 180 hours of xenon exposure. There is a clear indication of carbonyl group formation marked by a distinct peak in the 3340 cm^{-1} region that appears after xenon arc lamp exposure.

Accordingly, carbonyl and hydroxyl indices were computed as mentioned before. Figure 3.13 shows carbonyl index values obtained after xenon arc lamp exposure of PP filaments with 1 % of TDPA and ECM additives. It was observed that as the duration of xenon arc lamp increases, the value of carbonyl index increases. 100 % PP filaments showed a 230 % increase in carbonyl index after xenon arc lamp exposure. This can be explained as follows. The initial stage of photooxidation of polypropylene samples is the formation of radicals due to photo physical processes. The reaction of oxygen with these radicals leads to the formation of hydroperoxides that are unstable toward heat and UV light. They

decompose to free radicals, which in turn cause chain scissions. During this time Norrish I, II mechanisms are involved which lead to formation of oxidation products such as carbonyl compounds. Further oxidation of these carbonyl groups yields carboxylic acids. Furthermore intramolecular hydroperoxide decomposition reaction may occur and cause formation of vinyl groups. [91]. In case of TDPA containing samples, typical carbonyl absorption bands can be observed in the original samples, thus indicating the oxidative functionalization of the PP-TDPA, as a consequence of the thermo-oxidative degradation. 1% TDPA additive containing samples showed a 53% increase in carbonyl index after 180 hour xenon exposure. However, 2 % TDPA additive containing samples recorded almost a 213% increase in carbonyl index after 180 hours of xenon exposure. This increase in carbonyl index is clearly indicative of the occurrence of oxidative degradation accelerated by TDPA additives. A similar increase in carbonyl index was also observed in ECM additive containing samples. While the usage of 1% of ECM 0702 resulted in a 10% increase in carbonyl index after 180 hours of xenon arc lamp exposure, a 2% usage of ECM 0702 resulted in a 100 % increase in carbonyl index after 180 hour of xenon arc lamp exposure. This clearly shows that in case of ECM additives, as the concentration of additive increases, the carbonyl index also correspondingly increases, thereby indicating the UV initiated oxidation of PP resulting in the formation of carbonyl group containing compounds like ketones, carboxylic acids. Thus it can be summarized that the exposure of PP filaments to UV causes oxidative degradation evidenced by a consistent increase in carbonyl index noted in all samples.

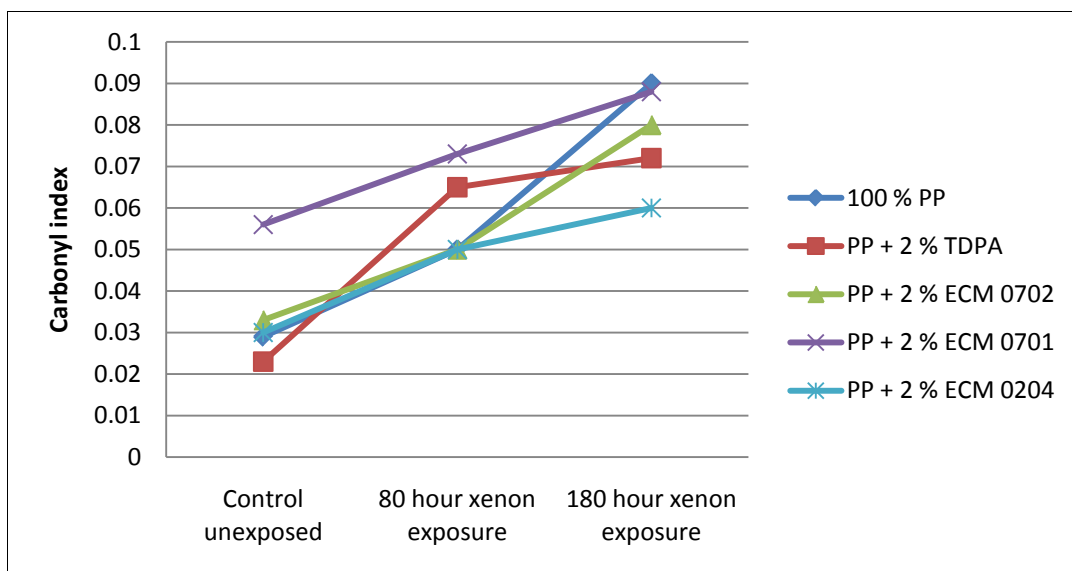


Figure 3.15. Carbonyl index for 2 % TDPA and ECM additive containing filaments for 0, 80 and 180 hours of xenon exposure.

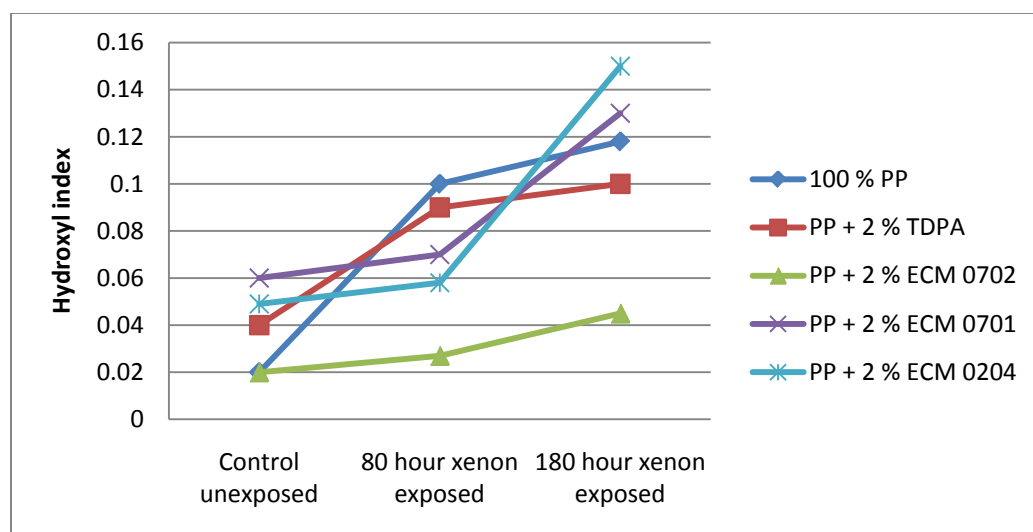


Figure 3.16. Hydroxyl index for 2 % TDPA and ECM additive containing filaments for 0, 80 and 180 hours of xenon exposure.

The degradation of polypropylene also results in the formation of hydroxyl products such as hydroperoxide, alcohols and carboxylic acid. This is indicated by an increase in the hydroxyl index as shown in Figure 3.16 and Figure 3.14.

3.1.5. SEM Imaging of polypropylene filaments with TDPA and ECM additives after xenon exposure

SEM analysis was carried out in order to study the effect of xenon exposure on the surface morphology of the filaments. In general, it can be observed that the exposing the samples to xenon results in significant surface deterioration. This is clearly illustrated in Figure 3.17 and 3.19. It is characterized by the formation of a net of spontaneous cracks on the sample surfaces which caused the embrittlement of the material.

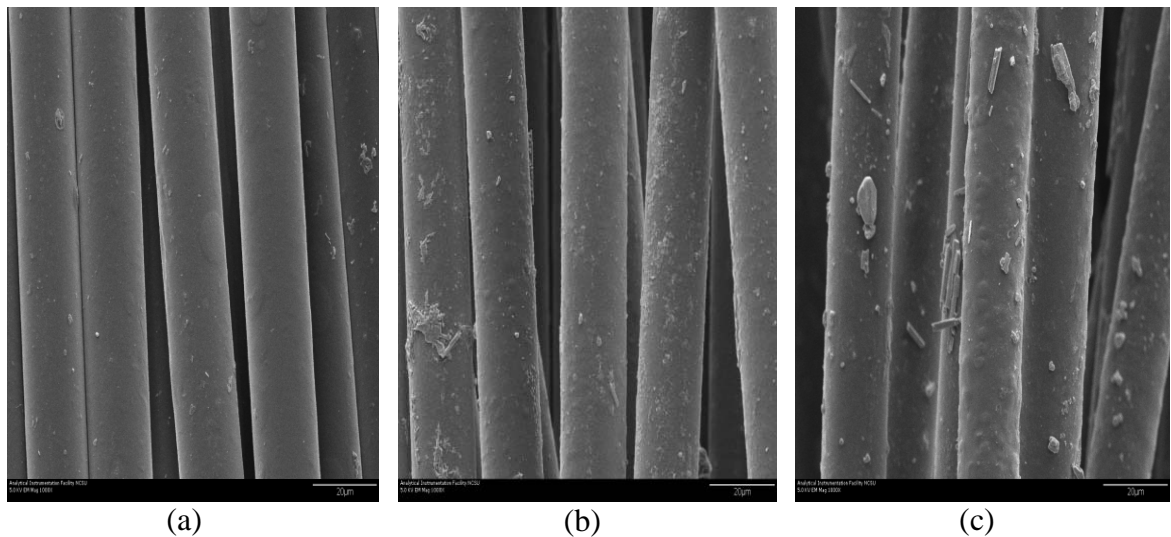


Figure 3.17. SEM micrographs of (a) Unexposed 100 % PP filament, (b) 100 % PP filament after 80 hour xenon exposure, (c) 100 % PP filament after 180 hour xenon exposure.

In case of 100 % PP filaments, it can be observed that the initial degradation begins with the formation of surface flakes. The nature of degradation is however not very extensive as compared to the additive containing filaments.

Filaments with 2 % TDPA show the presence of heavy surface deterioration coupled with crack formation after 180 Hour xenon exposure (Figure 3.18). Surface cracks sometimes form spontaneously during UV exposure as a result of the increase in crystallinity at the surface layers which leads to shrinkage. This process, called chemi-crystallization [93].

This may have contributed to the large loss in tensile properties observed in these filaments. By consequence, the photooxidation develops in an affected surface layer.

They appear firstly on the edges and propagate towards the center of sample surface. In the case of ECM additive containing samples, the degradation seems to be restrictive more to the surface. This is very clearly indicated in the Figure 3.19 (b, c, d). Though a very extensive surface crack formation seems to have occurred, the inner surface of the filaments is relatively less affected. This also being reflected in the tensile properties of this particular filament. It has been illustrated that the reduction in tensile strength of these filaments is not as prominent as in TDPA additive containing samples.

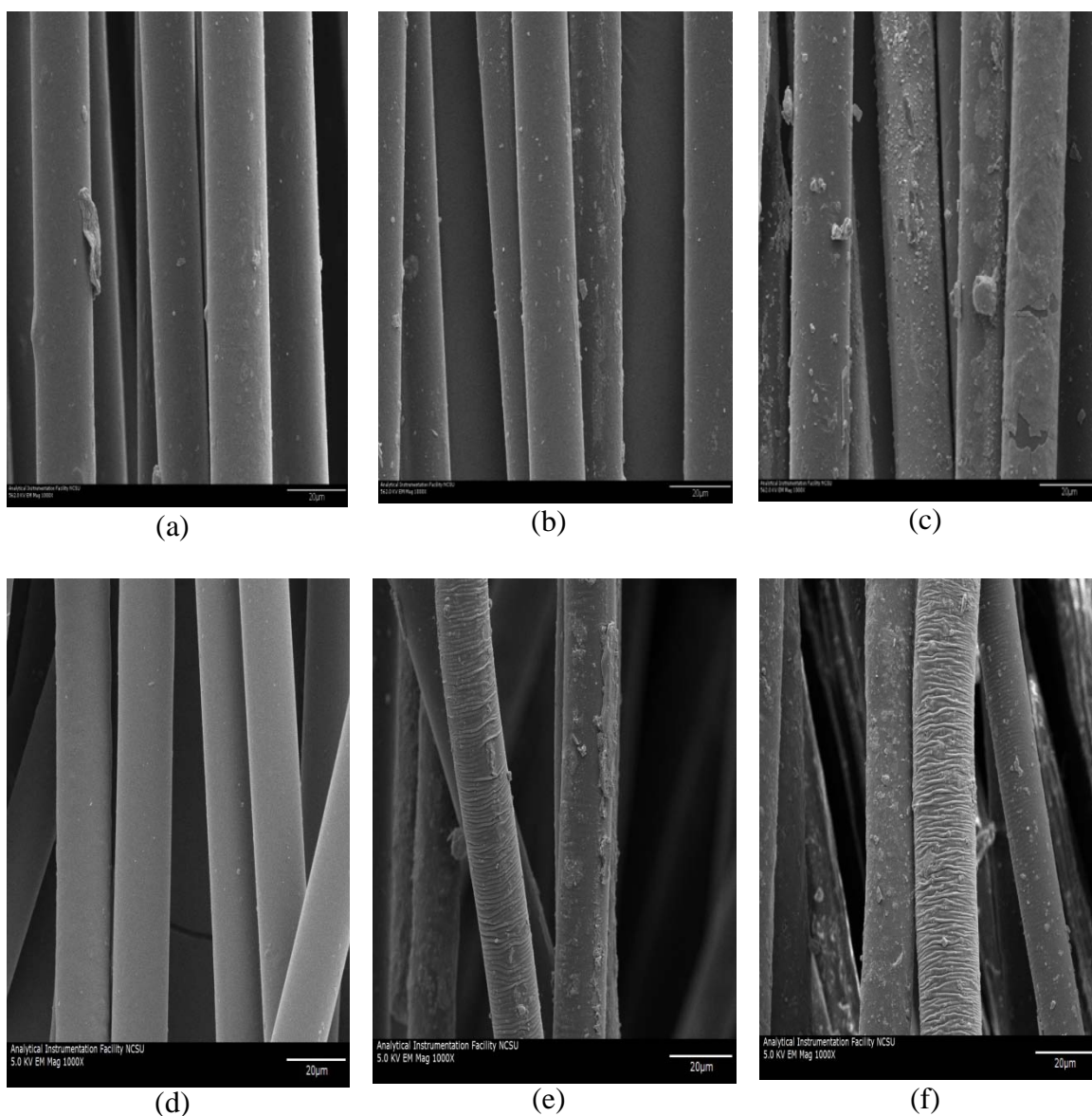


Figure 3.18. SEM micrographs of (a) Unexposed PP with 2% TDPA additive, (b) PP with 2 % TDPA after 80 hour xenon exposure, (c) PP with 2 % TDPA additive after 180 Hour xenon exposure, (d) Unexposed PP with 2% ECM 0702 additive, (e) PP with 2 % ECM 0702 additive after 80 hour. xenon exposure, (f) PP with 2 % ECM 0702 additive after 180 hour xenon exposure.

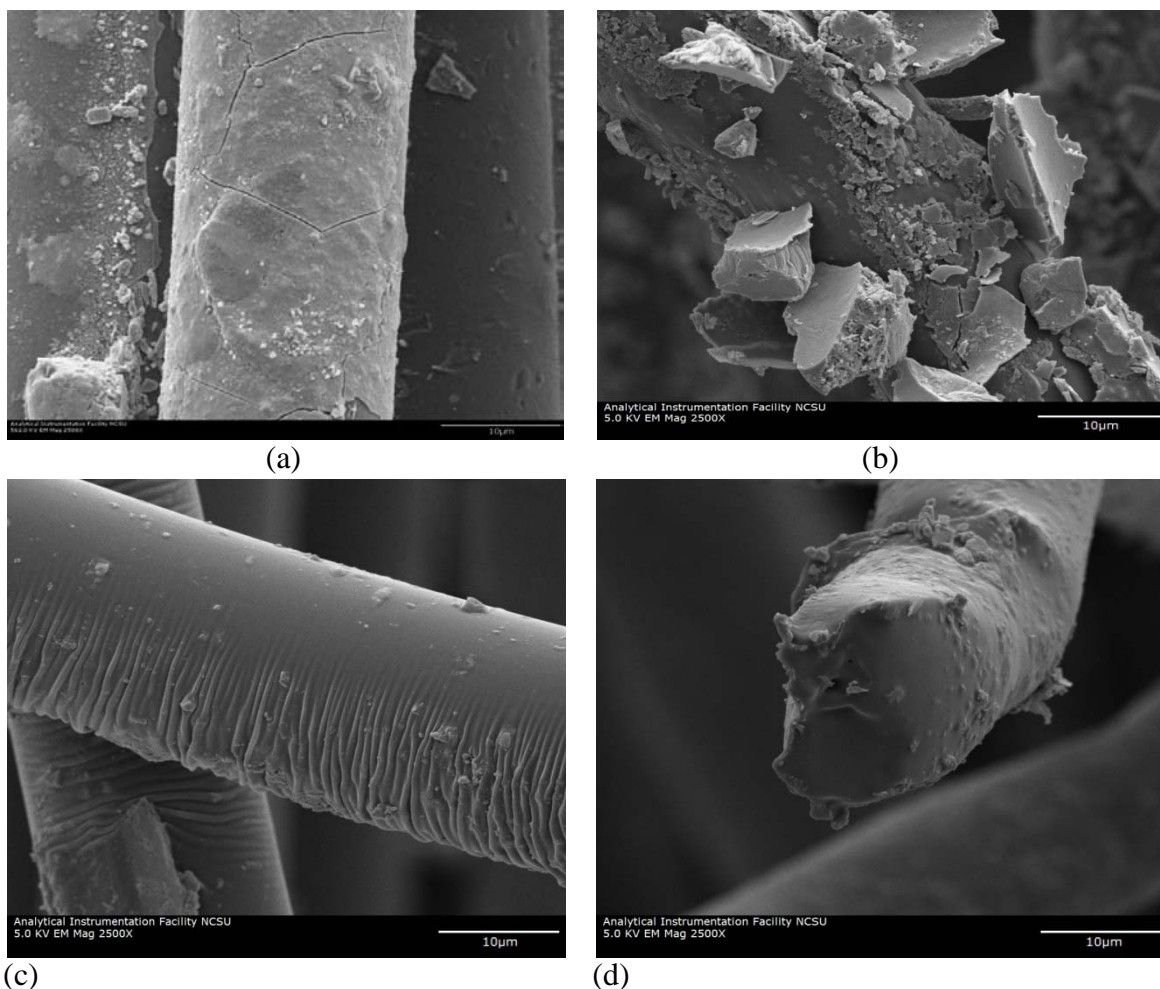


Figure 3.19. SEM micrographs of (a) PP filaments with 2% TDPA additive after 180 hour xenon exposure, (b), (c), (d) PP filaments with 2 % ECM 0204 after 180 hour xenon exposure.

The direction of xenon exposure also seems to have played an important role in the deterioration of samples. As seen in Figure 3.19(c), there is a clear distinction in the surface morphology of the same fiber. The exposed part of the filament is marked by the presence of extensive wrinkles whereas the unexposed part of the filament was still intact. Though precautions were taken to mount the samples on the sample holder as flat

as possible, slight overlapping of the individual filaments may lead to certain portions remaining unexposed which still contribute to the strength of the fibers. This may be one of the reasons causing high variation in the xenon exposed samples in particular. A possible explanation is that near the exposed side, the degradation is more rapid, whereas on the other side of the filament the action of UV is lesser. This kind of preferential degradation is more critical from a fracture mechanics standpoint. This could have been responsible for the large variation in tensile results. It was observed that the photooxidation ageing, (initiated by UV) though macroscopically heterogeneous, leads to formation of surface cracks. It is quite possible that these cracks may have propagated into the sample thereby exposing more surface area to UV action.

3. 2 CHARACTERIZATION OF SPUN BOND POLYPROPYLENE NONWOVENS CONTAINING TDPA AND ECM ADDITIVES

3.2.1. Manufacture of Spun Bond Polypropylene Nonwovens with TDPA and ECM additives

Manufacture of spunbond polypropylene nonwovens with 2 % additives was carried out at the Pilot Plant Facility at NCSU. Spunbond nonwovens of approximately 30 gsm were manufactured with a throughput of 0.6ghm (grams/hole/min) at a spin head temperature of 466 °F. In order to provide coherence to the web, the web was calendared by passage between calender rollers with a pressure of 750 psi. Bonding point was achieved by fusion of filament at their cross-over points between the raised patterns of a calender due to direct conduction of heat and pressure of the calendar. This type of bonding lead to a formation of bonding “points” or “spots” on the fabric. However, it was not possible to make nonwovens containing ECM 0701 additives even after repeated attempts. They showed problems in drawing and resulted in formation of loose mass of fibers instead of nonwoven webs and had no cohesion. To summarize, the following samples were tested:

- 1) Control PP
- 2) PP + TDPA (2 %)
- 3) PP + ECM 0702 (2%)
- 4) PP + ECM 0404 (2%)
- 5) PP + ECM 0204 (2%)

3.2.2. Preliminary characterization of polypropylene spunbond nonwovens with TDPA and ECM additives

Before proceeding with the degradation testing of nonwovens, it was necessary to characterize the nonwovens for their basic structural properties so that any chance of introduction of bias due to non-uniformity of samples could be eliminated. Hence the nonwovens were subjected to preliminary analysis to compare their basis weights, thickness and flexural rigidity

Table 4 shows the basis weight, thickness, flexural rigidity of the nonwovens.

Table 4. Physical properties of PP nonwovens with TDPA and ECM additives.

Type of Nonwoven	Basis Weight (grams/m ²)		Thickness (mm)		Flexural Rigidity (10 ⁵ Nm) (ASTM D 5732)	
	Mean	Standard Deviation	Mean	Standard Deviation	Mean	Standard Deviation
Control PP NW	29.8	0.1	0.215	0.3	2.59	0.3
PP + 2 % TDPA	30.1	0.4	0.220	0.2	2.67	0.5
PP + 2 % ECM 0702	29.76	0.2	0.213	0.4	2.63	0.5
PP + 2 % ECM 0204	30.20	0.5	0.219	0.6	2.58	0.6
PP + 2 % ECM 0404	30.17	0.1	0.221	0.1	2.61	0.8

Having ensured that the nonwovens had similar physical properties, three types of degradation studies were carried out on the nonwovens namely:

- 1) Xenon exposure
- 2) Vermicomposting studies
- 3) Soil burial studies

Each of these sections will be discussed in detail. After degradation studies, the samples were analyzed for their tensile properties. FTIR and SEM imaging was also carried out.

3.2.3. Characterization of the PP Spunbond Nonwovens with TDPA and ECM additives after xenon exposure

3.2.3.1. Tensile testing of PP spunbond nonwovens with TDPA and ECM additives after xenon exposure

Tensile testing of PP nonwoven samples was carried out after xenon exposure. Figure 3.20 below shows the values for elongation and modulus for these samples before and after xenon exposure:

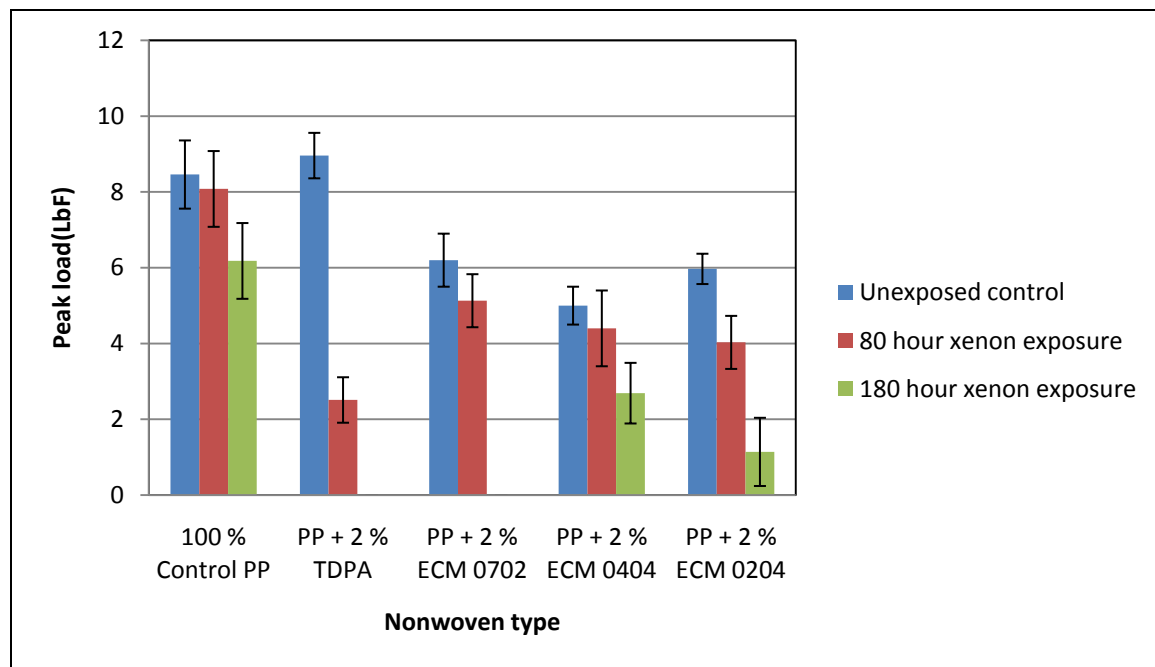


Figure 3.20. Peak load values in the Machine direction for TDPA and ECM containing nonwovens for 0, 80, 180 hours of xenon exposure.

It was observed that all the samples show significant reduction in strength (peak load) on UV exposure. This reduction in elongation is especially significant in samples containing TDPA additives, after just 80 hours xenon arc exposure.

In case of 100 % control PP samples there is a 26 % reduction in peak load after 180 hours of xenon exposure. This reduction can be attributed to the chain cleavage that occurs due to exposure to UV. UV exposure causes the oxidation of polypropylene which results in hydroperoxide formation. Hydroperoxide photocleavage results in the formation of reactive macroalkoxy radical. The macroalkoxy radical plays a central role in the deterioration of the mechanical properties of polyolefins.[28,29]

Extensive entanglement of polymer segments in the amorphous zones between crystallites is believed to be essential to ensure tough, extensible films, and backbone integrity is essential for tough, oriented fibers. Only the amorphous zones of polypropylene are readily penetrable. Hence it can be concluded that all of the observed photooxidation damage is concentrated in this region. Thus the backbone cleavage which occurs from up to 50% of the alkoxy radicals in PP must have lead to the catastrophic deterioration in tensile properties that results, after a critical degree of photooxidation was achieved. [29]

In case of TDPA additive containing samples, the reduction in mechanical properties was very evident. After a mere 80 Hour xenon exposure, a 72 % decrease in peak load in samples was observed. TDPA additive containing nonwovens degraded to such an extent

that samples obtained after 180 hours UV exposure crumbled on touching and were too weak to even be mounted on the tensile testing machine. This is indicated by the absence of readings in the bar graphs for 180 xenon exposed samples. The substantial drop in peak load is indicative of strength loss and hence it can be inferred that additive containing samples degenerate to a larger extent. The patent issued from EPI Inc. speaks of a “degradable/compostable additive packages for adding to polyolefin resins used in the manufacture of packaging materials to make the specific packaging product degradable/compostable”[70] . It indicates the presence of metal stearates. It has been proved that these stearates are widely used as pro-degradants due to the ability of the transition metal to switch between two oxidation states, which can in the process, lead to the decomposition of hydroperoxides. The decomposition of hydroperoxides subsequently leads to the formation of carbonyl groups, which can act as reactive centers for the photolytic cleavage of the polymeric backbone by Norrish reactions of type I, II and III. This may explain the catastrophic deterioration in tensile properties which has been observed in TDPA containing samples.

In ECM additive containing nonwoven samples, a similar trend was observed. Though they had initial tensile strengths of lesser magnitude than PP and TDPA additive containing ones, it can be observed that they do show the trend of drastic drop in peak load after xenon exposure. As evident from the tensile data in Figure 3.20, ECM 0702 containing samples show maximum degradation with 180 hour xenon exposure with samples being too weak to be tested for their mechanical properties. The samples with

ECM 0204 and ECM 0404 show an approximate 46 % and 81 % reduction in peak load respectively on 180 hours of xenon exposure. Figure 3.21 illustrates the effect of xenon exposure on elongation (%) properties of the nonwovens.

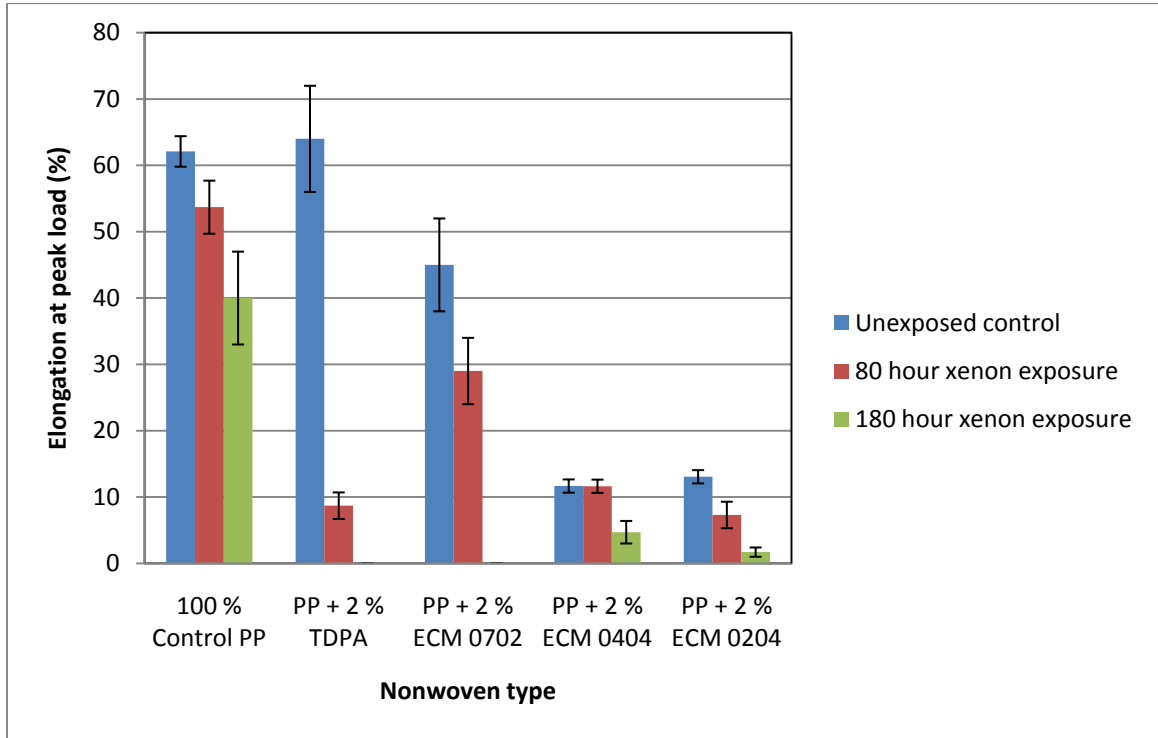


Figure 3.21. Elongation at peak load (%) values in the machine direction for TDPA and ECM containing nonwovens for 0, 80, 180 hours of xenon exposure.

Rapid drop in elongation at break is associated with the formation of surface cracks. PP is notch sensitive. Hence the presence of thin oxidized surface layers which are already cracked leads to complete failure when the samples are stretched during tensile testing. This trend of reduction in elongation at peak load has been exhibited in all samples with a maximum reduction being recorded in TDPA containing samples.

It was observed that some of the exposed samples showed high coefficient of variation in elongation after xenon exposure (17% in control PP, and 36 % in ECM 0204 containing samples after 180 hr xenon exposure). The high variation may be attributed to the large non-uniformity which is present inherently in the nonwoven webs. Nonwoven fabrics often display anisotropic behavior with variations in properties across the width and length of the web. Unevenness is usually caused by the aerodynamic filament drawing and web formation, the mode of bonding also playing an important role. Further degradation by UV exposure might have been instrumental in increasing the C.V. in these samples.

3.2.3.2. FTIR of nonwovens containing TDP and ECM additives after xenon exposure

Photooxidation of polypropylene produces a complex range of carbonyl species.

Oxidation, long wavelength initiated photooxidation of PP gives hydroperoxide groups (PPOOH) as the major product, together with lesser amounts of alcohol, carbonyl, and peroxide groups. All three sources of initiation give essentially the same product distribution [29, 14]

Carlsson and Wiles [14] attempted to characterize the carbonyl products from PPOOH photolysis and concluded that ketones dominate, with decreasing amounts of carboxylic acid, esters, unsaturated acids, peracids, peresters, and aldehydes.

Although there is a very large uncertainty in the importance of the last five products, the IR absorptions resulting from ketones (at 1718 cm^{-1} and 1726 cm^{-1} in hydrocarbons) are

prominent. Photooxidation results in the formation of large number of carbonyl products, which can usually be located at 1600 cm^{-1} on an IR spectrum (Figure 3.17).

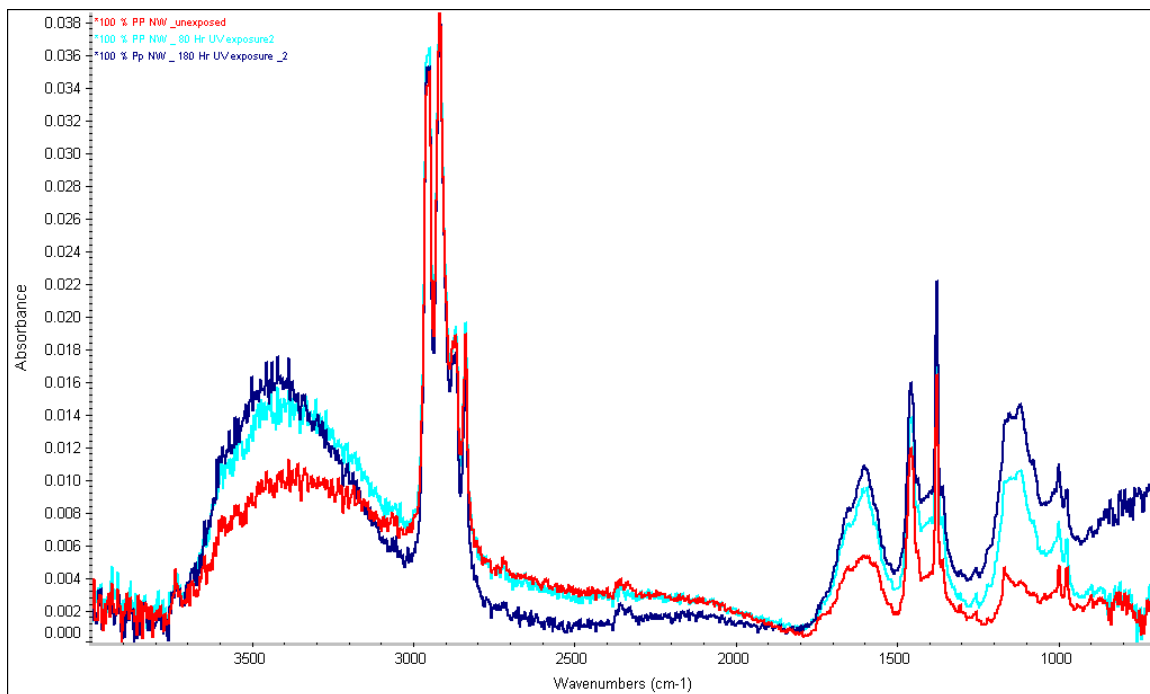


Figure 3.22. FTIR spectrum of 100 % PP nonwovens after 0, 80 and 180 hour xenon exposure.

Photodegradation is also accompanied by the formation of hydroperoxides as shown by the infrared (IR) spectral changes at 3400 cm^{-1} (Figure 3.17).

IR absorption predominantly results from these hydroperoxide groups ($-\text{OOH}$), and the carbonyl groups ($>\text{C}=\text{O}$). The kinetic build up of $>\text{C}=\text{O}$ products is very similar to the $-\text{HOO}$ build up. As before, carbonyl index was calculated as a ratio of absorbance at 1610 cm^{-1} (corresponding to the carbonyl peak) to the absorbance at 2920 cm^{-1}

(corresponding to the C-H peak) . Hydroxyl index was calculated as a ratio of absorbance at 3340 cm^{-1} (corresponding to the carbonyl peak) to the absorbance at 2920 cm^{-1} .

Figure 3.23 shows the increase in carbonyl index noted in nonwoven samples after 0, 80 and 180 hours of xenon exposure.

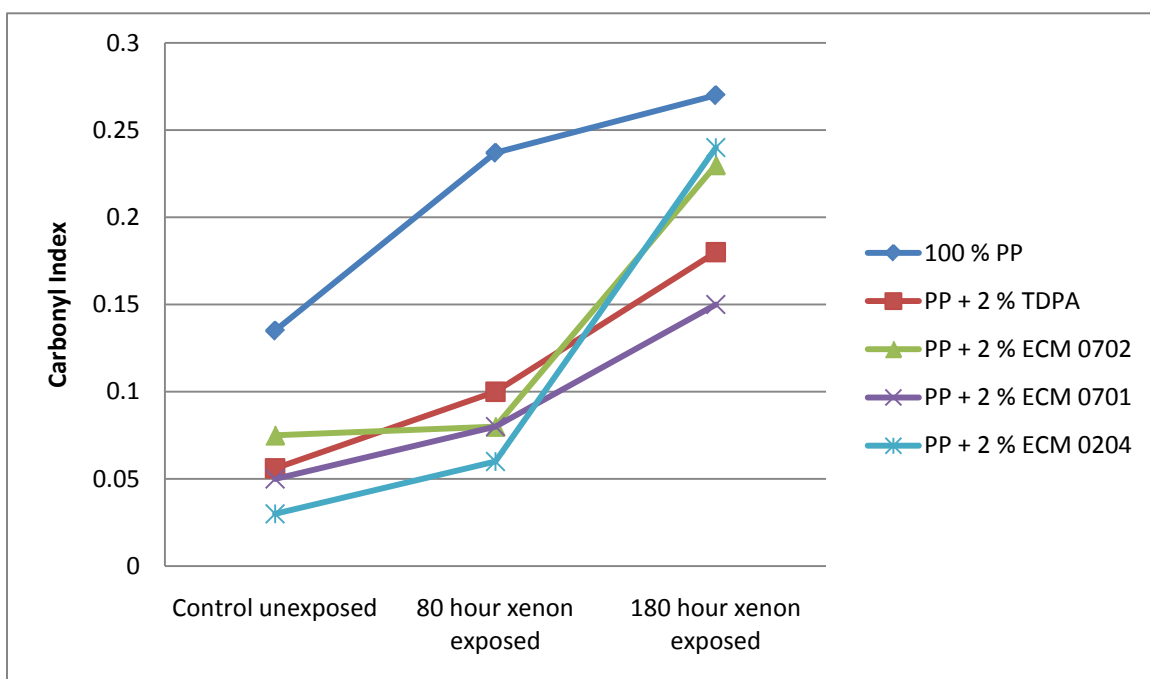


Figure 3.23. Carbonyl index for TDPA and ECM additive containing nonwovens for 0, 80 and 180 hours of xenon exposure.

As seen in Figure 3.23, there is a sharp increase in carbonyl index noted after xenon exposure. This increase is especially significant after 180 hour xenon exposure, which is indicated by the steep slope in all the samples between 80 and 180 hour xenon exposure.

Previous studies carried out by Adams et al on photooxidized PP sheets found a significant presence of alcohol and carbonyl groups. The carbonyl groups were reported to result from concentrations of ester, acid, ketone, aldehyde and lactone [94]. The steep increase in the carbonyl index of the present studies clearly indicates the presence of these compounds that may have been generated due to the from the beta scission of macroalkoxy radicals or from peroxy radical cross termination.

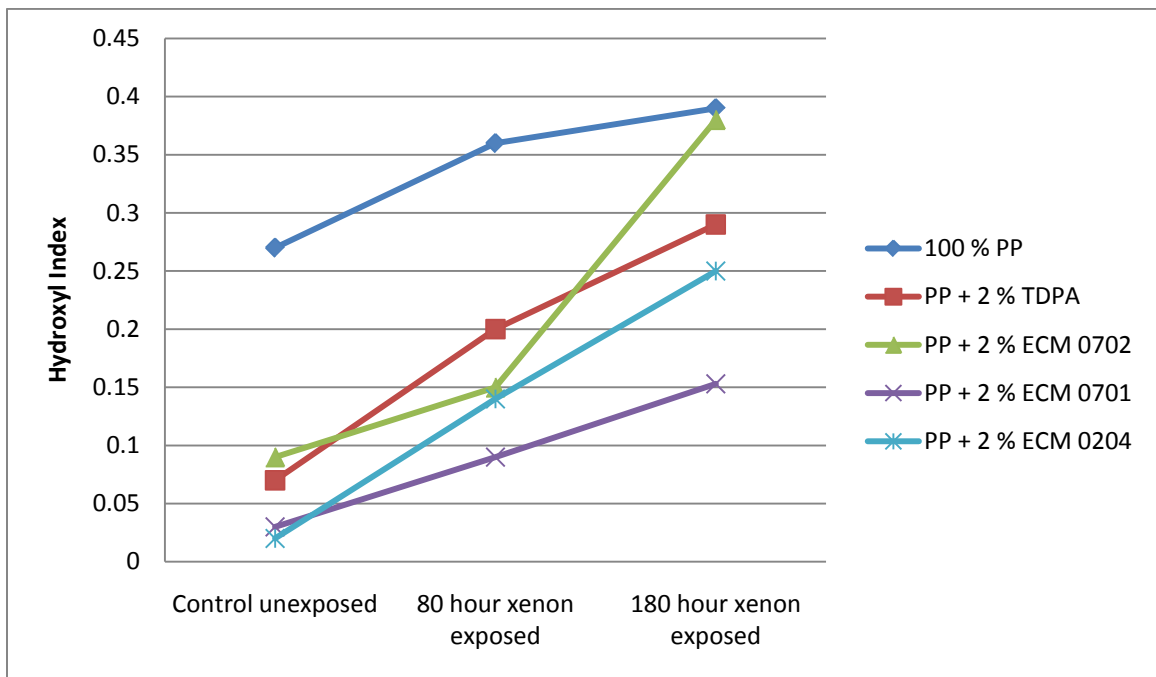


Figure 3.24. Hydroxyl index for TDPA and ECM additive containing nonwovens for 0, 80 and 180 hours of xenon exposure.

Figure 3.24 illustrates the increase in hydroxyl index after xenon exposure. This increase, especially after 180 hour xenon exposure shows the formation of hydroxyl containing compounds which are formed due to the oxidation of polypropylene. As indicated, as the

duration of xenon exposure increases, the hydroxyl index also increases rapidly thereby verifying the photooxidation of polypropylene.

3.2.3.3. SEM imaging of PP nonwovens containing TDPA and ECM additives after xenon exposure

SEM analysis of the samples was carried out in order to study the effect of xenon exposure on the surface morphology of the filaments. In general, it can be observed that the exposing the samples to xenon results in tremendous surface deterioration.

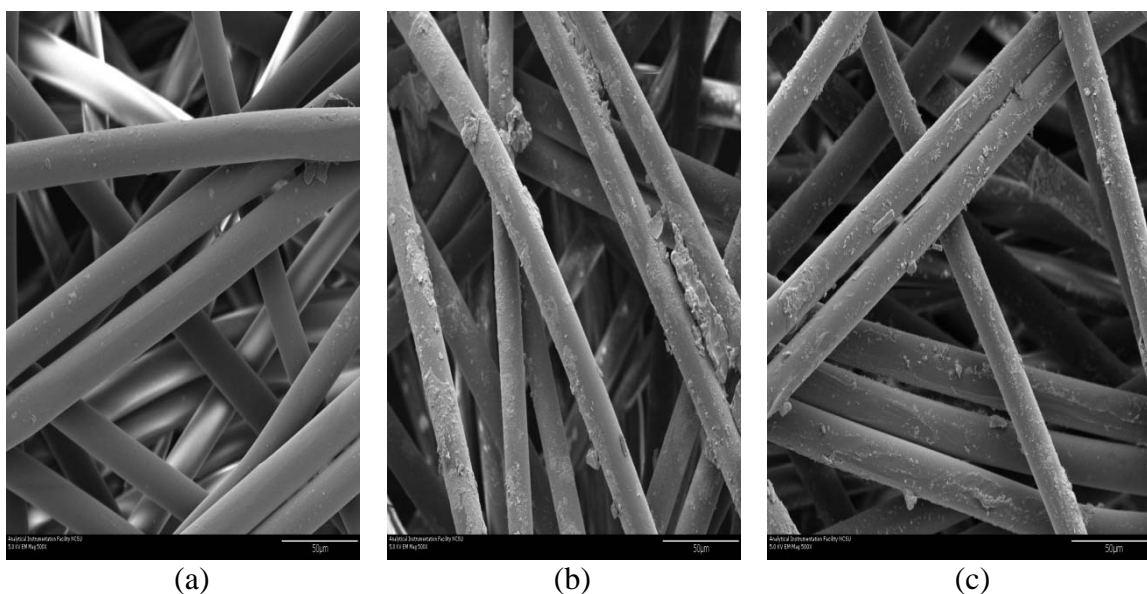


Figure 3.25. SEM micrographs of (a) Unexposed 100 % PP nonwoven , (b) 100 % PP Nonwoven after 80 hour xenon exposure, (c) 100 % PP nonwoven after 180 hour xenon exposure.

In case of 100 % polypropylene samples, the degradation was marked by the presence of surface flakes. The relatively smooth fibers in the unexposed PP nonwovens, became rougher , distinctly showing the presence of surface abrasion and outer surface

deterioration. However, the nature of this degradation was not very extensive as compared to the additive containing nonwovens. This is evident from Figure 3.25.

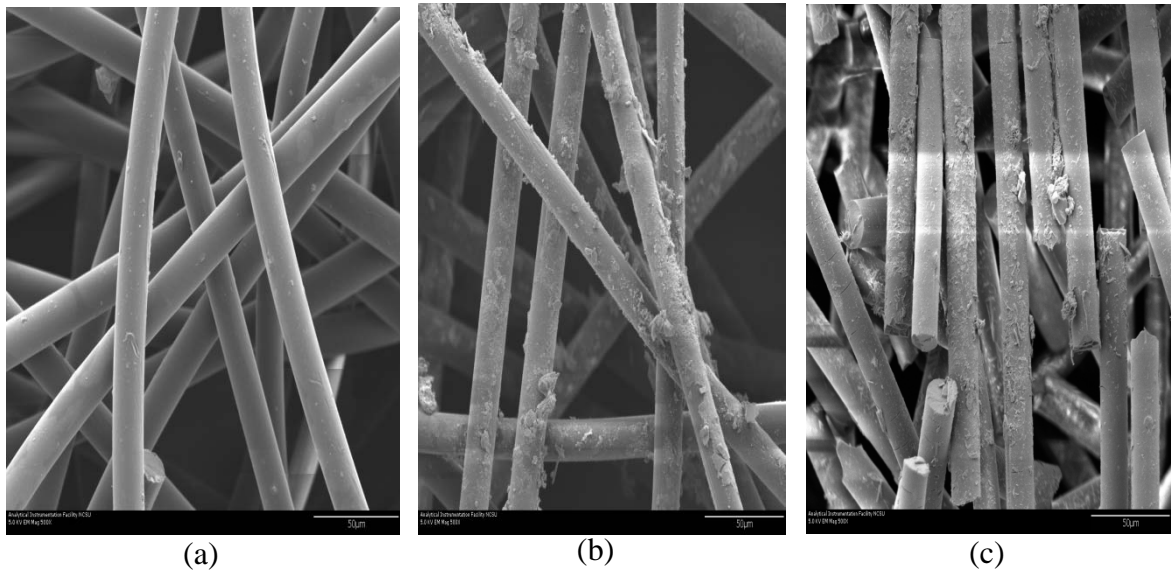
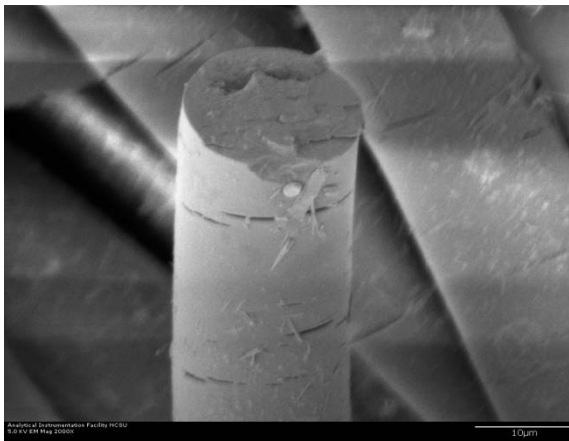


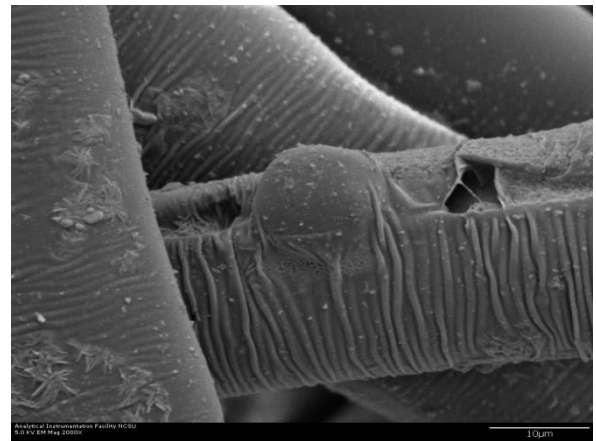
Figure 3.26. SEM micrographs of (a) Unexposed PP nonwovens with 2% TDPA additive, (b) PP nonwovens with 2 % TDPA after 80 hour xenon exposure, (c) PP nonwovens with 2 % TDPA additive after 180 hour xenon exposure.

In 2 % TDPA containing nonwovens, the degradation due to xenon exposure has been extensive, resulting in the formation of extensive cracks which is prominent after mere 80 hour xenon exposure. Further exposure lead to even more degradation which was marked by the presence of individual fiber degradation with chopped strands being present (Figure 3.26 c). It is the presence of these chopped fibers which must have lead to the catastrophic decrease in mechanical properties to such an extent that the nonwoven had no structural integrity and collapsed on mere touch. A further magnification of these fibers indicated that the degradation was not just limited to the surface but also the interior. As shown in the Figure 3.27 (b) below, the breakage of individual fibers may

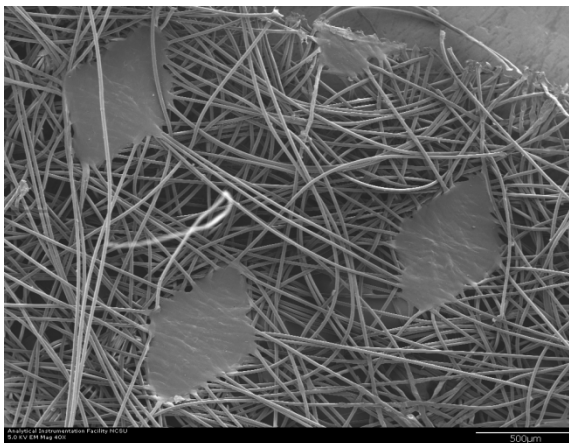
have lead to more area being exposed to xenon thereby resulting in degradation even within the interior of the fibers of the nonwoven. This may be responsible for the acute reduction in tensile properties at higher exposure times.



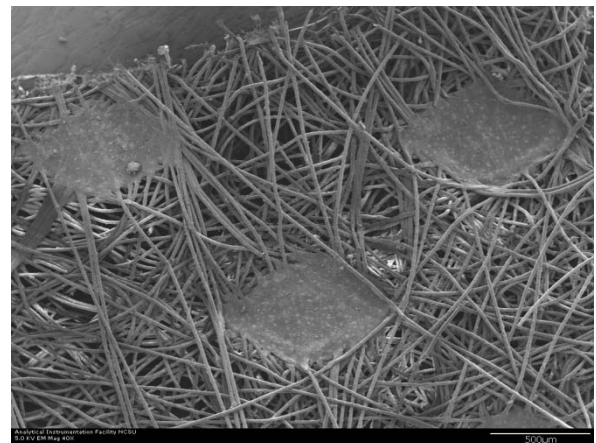
(a)



(b)



(c)



(d)

Figure 3.27. SEM micrographs of (a), (b) PP nonwovens with 2% TDPA additive after 180 hour xenon exposure, (c) Bond points in control PP nonwoven with 2 % TDPA (d) Bond points in control PP nonwoven with 2 % TDPA after 180 hour xenon exposure.

The bond points in a nonwoven play an important role in imparting structural integrity strength and coherence to the nonwoven web. An SEM study of the bondpoints of the nonwoven was conducted to analyse their degradation on xenon exposure. As seen in the Figure 3.27 (d), the unexposed samples are marked by clear bond points with a smooth appearance. However, in the exposed samples there is evident tearing apart of fibers from the bondpoints coupled with crack formation after 180 hour xenon exposure. This deterioration of the bond points may also have had a significant role to play in the drastic drop in tensile strength of the nonwoven after xenon exposure.

3.2.4. Characterization of Spunbond PP Nonwovens with additives after Vermicomposting

Vermicomposting of the PP spunbond nonwovens was carried out to compare the degradation caused by xenon against composting by earthworms. This composting study, as stated before, was conducted at the NCSU composting facilities for a duration of 4 weeks. A weight change analysis was carried out to monitor any changes in weight. However, there was no marked change in weight of the vermicomposted nonwovens in the samples (rounded to last four decimals in grams). Subsequently the following characterization was carried out.

3.2.4.1. *Tensile testing of PP Nonwovens with TDPA and ECM additives after vermicomposting*

The tensile testing of vermicomposted samples was conducted in order to estimate whether the action of earthworms had any effect on the compostability of the polypropylene nonwovens.

The idea behind this compostability test was that certain species of earthworms can consume organic residuals very rapidly and fragment them into much finer particles by passing them through their grinding gizzard. Figure 3.28 shows the effect of vermicomposting on the tensile properties of nonwovens containing additives. As observed, all the nonwoven samples showed a reduction in average peak load values after 4 weeks of vermicomposting.

However the decrease in average strength in 100 % control polypropylene is pronounced with almost an 18 % reduction in peak load values after a 4 week vermicomposting treatment. However considering the overlapping of the error bars, the decrease in peak load cannot be said to be significant.

A similar decrease of 18 % in peak loads was observed in TDPA additive containing nonwovens too. However, in case of ECM additive containing nonwovens, the reduction in peak load is much more significant. Nonwovens with ECM 0702 additive showed a 28% reduction in peak load after 4 week vermicomposting whereas additives with ECM 0404 showed a 19 % reduction in peak load.

The action of earthworms in vermicomposting is both physical/mechanical and biochemical. Physical participation in degrading organic substrates results in

fragmentation, thereby increasing the surface area of action, turnover and aeration [95]. It is this physical degradation that may have been responsible for the reduction in tensile properties of the nonwovens. Overall it was observed that the samples do show slightly high standard deviation. This may be attributed to the large variation present in the nonwoven web itself due to the random orientation of fibers in the nonwovens.

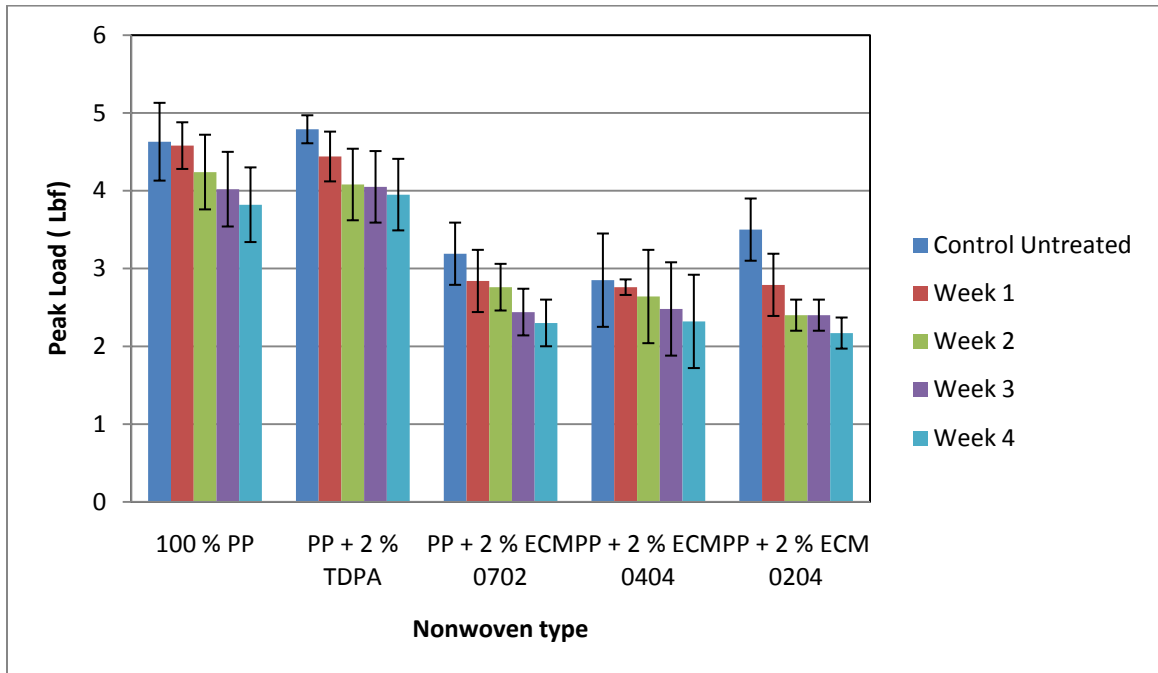


Figure 3.28. Peak load values in the cross direction for TDPA and ECM containing nonwovens after 4 week vermicomposting.

However, as compared to xenon exposure, this decrease in tensile properties is not very prominent. It can be explained by the fact that the phenomenal decrease in tensile strength of xenon exposed samples is due to the beta scission of the backbone chain of

polypropylene. The photo initiation of this oxidation of polypropylene is of paramount importance. In absence of UV, the efficiency of initiating oxidation chains will be much lower. Carlsson et al has shown that for commercial PP film and fibers that have not been previously UV exposed, and are free of deliberately added dyes and pigments, initiation by generation of free radicals decreases [96]. In case of vermicomposting, the samples were buried in a composting pit. The samples were not exposed to UV. This absence of UV exposure might have been the major reason for the tensile strengths not dropping significantly as compared to xenon exposed samples.

Also another factor to be considered is that though there is some loss of tensile strength seen due to joint action of earthworms and microorganism, vermicomposting does not involve a thermophilic stage. Though conditions of high humidity and temperatures of nearly 60- 77 °F were used, this is not sufficient enough to initiate thermal oxidation of polypropylene. In case of TDPA, the company speaks of a compostable package perhaps containing the presence of stearates. The principle of using transition metal ion stearates as an additive is that transition metals are able to switch between two oxidation states, which can in the process, lead to the decomposition of hydroperoxides. The decomposition of hydroperoxides subsequently leads to the formation of carbonyl groups, which can act as reactive centres for the photolytic cleavage of the polymeric backbone by Norrish reactions of type I, II and III [67]. However, this can occur only in the presence of an initiator like heat or light. Owing to the absence of using high temperature or UV exposure, it is quite possible that sufficient degradation may have not occurred as compared to UV exposed samples.

To sum up, it was observed that vermicomposting of polypropylene samples with additives did show a decrease in tensile properties after 4 weeks. This reduction may be attributed to the ability of the worms to consume organic residuals very rapidly and fragment them into much finer particles. However as compared to xenon exposure, the reduction is not very significant due to the absence of an initiator like UV or high temperature which can initiate the oxidation of polypropylene.

3.2.4.2. FTIR of PP Nonwovens with TDPA and ECM additives after vermicomposting

Literature suggests that the worms maintain aerobic conditions in the organic substances and accelerate and enhance the biological decomposition of the organic substances.

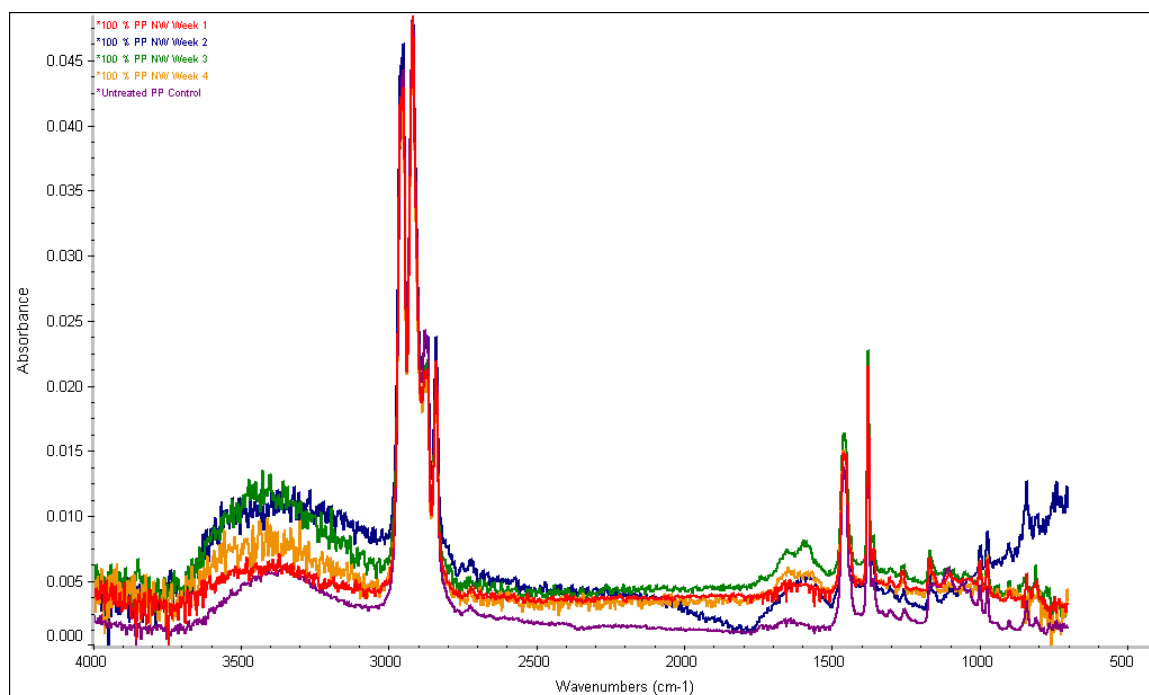


Figure 3.29. FTIR spectrum of PP nonwovens after 4 week vermicomposting.

Physical participation in degrading organic substrates results in fragmentation, thereby increasing the surface area of action, turnover and aeration. This can be seen by the slight reduction of tensile properties of nonwovens. However, apart from physical degradation there are also chemical and biochemical changes that occur on vermicomposting. These changes in the degradation of organic matter are carried out through enzymatic digestion, enrichment by nitrogen excrement and transport of organic and inorganic materials. In order to estimate this, FTIR of vermicomposted samples was done.

Carbonyl index was calculated as a ratio of absorbance at 1610 cm^{-1} (corresponding to the carbonyl peak) to the absorbance at 2920 cm^{-1} (corresponding to the C-H peak). hydroxyl index was calculated as a ratio of absorbance at 3340 cm^{-1} (corresponding to the carbonyl peak) to the absorbance at 2920 cm^{-1} . The Figure 3.30 shows the increase in carbonyl index noted in nonwoven samples after 4 weeks of vermicomposting.

In the vermicomposting process, worms are used to develop an optimum environment for consuming or metabolizing the biosolids and producing feces or castings. As members of the organic matter decomposer community, earthworms can assimilate carbon from the deposited organic matter fraction. Polypropylene is a polyolefin predominantly comprising carbon and hydrogen. Hence, the experiment was done to estimate whether the worms were able to assimilate carbon from polypropylene and convert them into organic biodegradable matter in the form of carboxylic acids, alcohols etc.

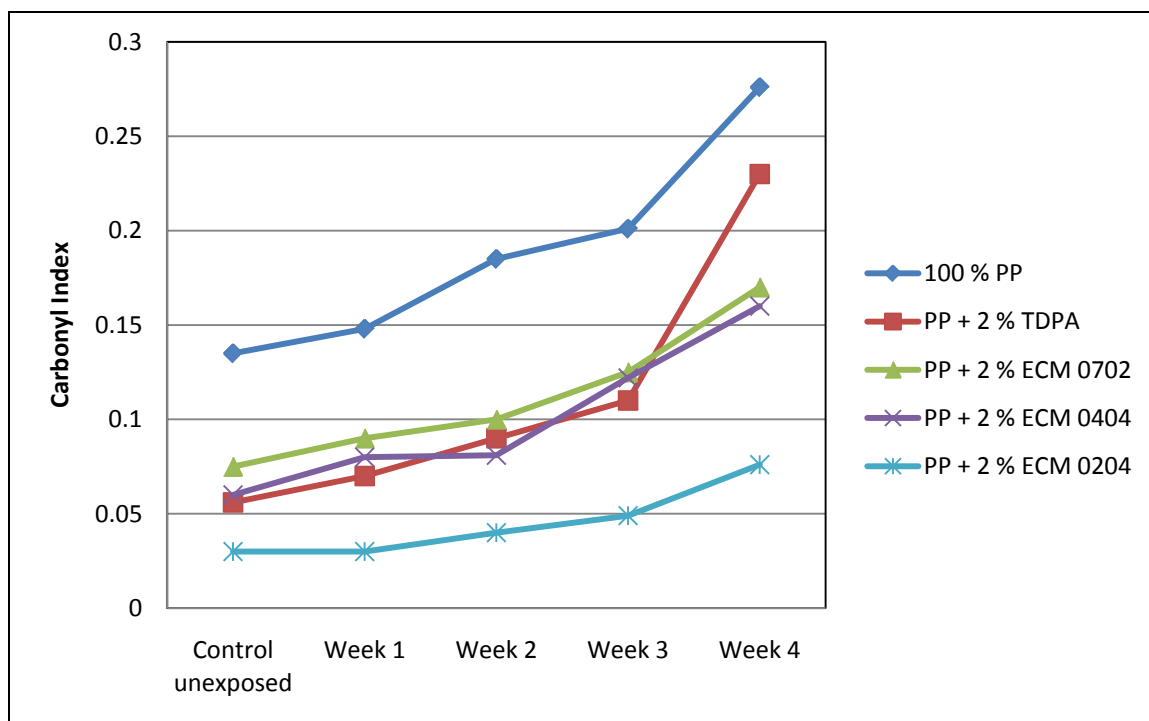


Figure 3.30. Carbonyl index values after 4 weeks of vermicomposting.

100 % PP samples showed a 300 % increase in carbonyl index after 4 weeks of vermicomposting as compared to a 125 % increase in carbonyl index in TDPA containing Nonwovens. In case of TDPA containing samples, a sudden increase was observed between the third and fourth week. Chiellini et al. has studied the biodegradability of films containing TDPA [61]. Cell enzymes are known to encourage peroxidation by the formation of free radical superoxide. When protonated, this superoxide is converted into the more reactive peroxy radical and hydrogen peroxide. The transition metal ions present in the additive can reduce these to give highly reactive hydroxy radical. Chiellini et al. states that it is these OH radicals that initiate further peroxidation leading to continued biodegradation and bioassimilation. Thus this increase in carbonyl index of

TDPA additive containing nonwovens can be attributed to the action of enzymes secreted by the fungi and earthworms present in the pit.

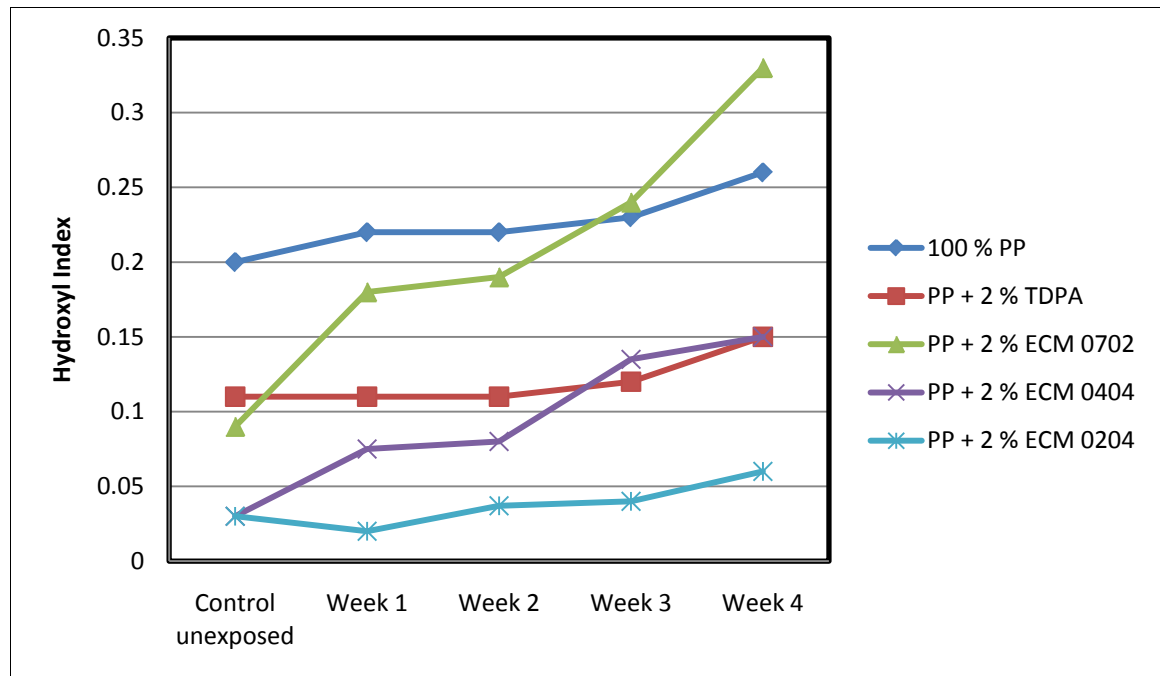


Figure 3.31. Hydroxyl index values after 4 weeks vermicomposting.

Also, between week 3 and week 4, in TDPA additive containing samples, a drastic increase of nearly 100 % in the carbonyl index has been observed. This could perhaps indicate the effect of the additive on the degradation of polypropylene. Since the test was conducted for a limited period of 4 weeks due to limited availability of the composting facilities, it is quite possible that more increase could have been noted in these samples. ECM additive containing samples showed a gradual increase in carbonyl index with

ECM 0702 showing a maximum increase of 125% in ECM 0702 additive containing samples.

The degradation of polypropylene also results in the formation of hydroxyl products such as hydroperoxide, alcohols and carboxylic acid. These are usually seen in the hydroxyl region of the spectra at an absorbance region of $3600 - 3200 \text{ cm}^{-1}$. Accordingly hydroxyl index was also computed for the vermicomposted samples. In all the samples there was a constant increase in the hydroxyl index on vermicomposting. This is shown in Figure 3.31.

Thus it can be said that the action of earthworms in this process is both physical/mechanical and biochemical. Physical participation in degrading organic substrates results in fragmentation, thereby increasing the surface area of action, turnover and aeration. Biochemical changes in the degradation of organic matter are carried out through enzymatic digestion, enrichment by nitrogen excrement and transport of organic and inorganic materials.

3.2.4.3. SEM of PP Nonwovens with TDPA and ECM additives after 4 week vermicomposting

SEM analysis of the nonwovens after 4 week vermicomposting was done in order to study the changes in morphology which may have occurred due to composting. Figure 3.27 shows the physical changes that took place in the nonwovens after 4 week vermicomposting.

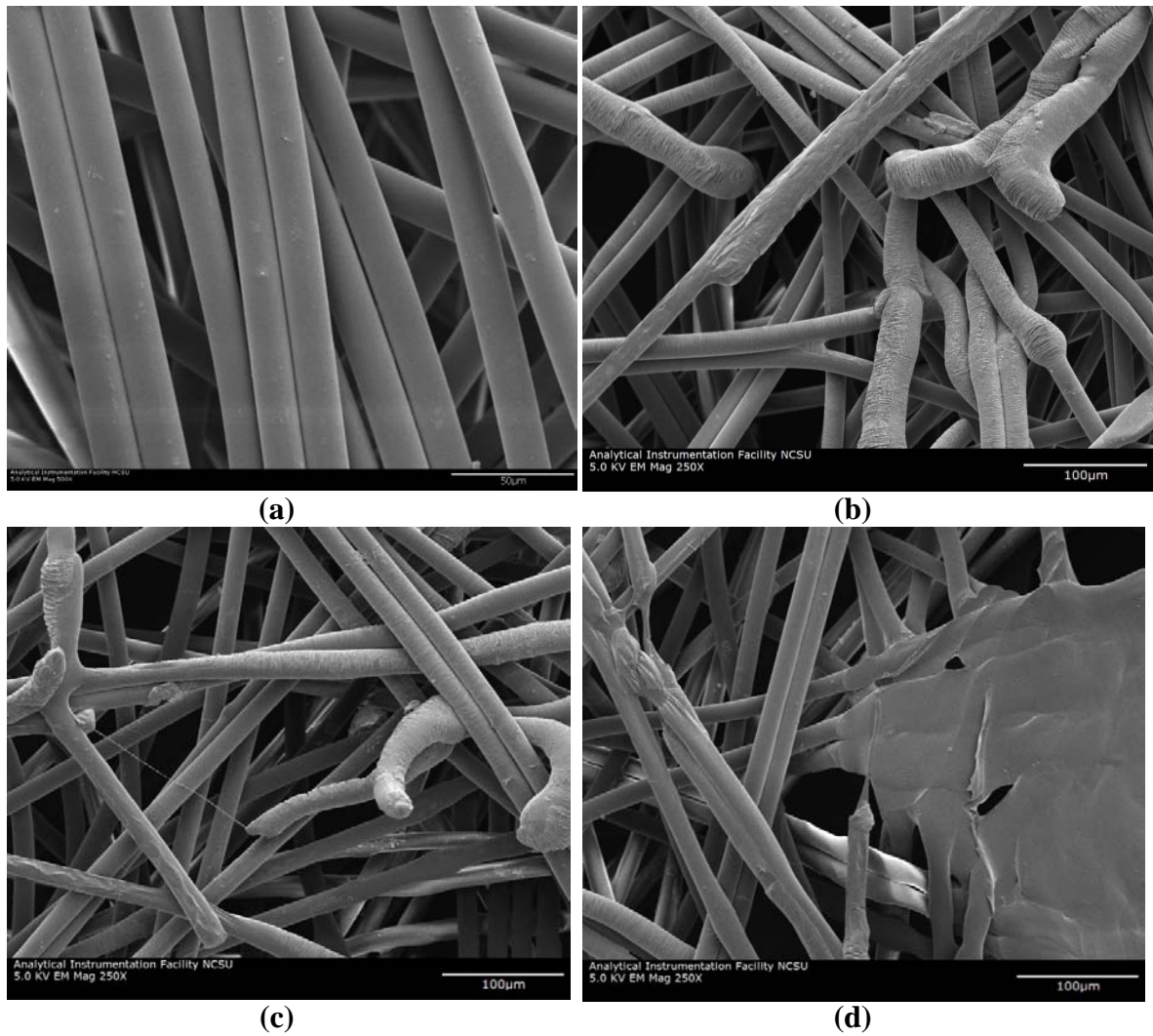


Figure 3.32. SEM micrographs of (a) Control 100 % PP nonwoven (b) 100% PP nonwoven after 4 week vermicomposting (c) PP nonwoven with 2 % TDPA after 4 week vermicomposting (d) Bond point in PP nonwoven with 2 % TDPA after 4 week vermicomposting.

The physical effect of the earthworms on the nonwovens was earlier estimated by the drop in tensile strengths. The SEM also indicates the physical degradation caused by earthworms. As seen in Figure 3.32 (b), after 4 weeks of vermicomposting, there is a

slight swelling of fibers observed with surface deterioration. There are also cut fibres with damage marked by the presence of ring like patterns on their surface. The same can also be observed in TDPA containing samples.

A further study of bondpoints was done. There is evident presence of fibers tearing off from the bond point which may have been due to the action of earthworms. In some samples, holes were present in the bonding regions. It is these holes which may have been responsible for the reduction in tensile properties. Also, the fibers around the bond points seem slightly damaged which may have further contributed to the lower peak loads recorded in these samples.

It was observed that all samples after 4 weeks of vermicomposting, recorded peak load values which were significantly higher than the peak load values obtained after xenon arc lamp exposure. For instance, TDPA containing samples showed a tensile peak load of 3.95 lbf after 4 weeks of vermicomposting. As against this, TDPA additive containing samples after 180 hours of xenon arc lamp exposure were so weak that they could not even be mounted on the tensile testing machine. However, if the respective carbonyl indices of these samples were to be compared, the carbonyl index obtained for TDPA containing samples after 4 weeks of soil burial (0.13) was approximately equal to the carbonyl index values obtained for TDPA containing samples after 180 hours of xenon exposure (0.18). This shows that though the nature of oxidation on the surface is similar in both cases, the extent of oxidative degradation that has occurred in xenon arc lamp exposed samples is much higher than the oxidation occurring in vermicomposted samples

which seems to be restricted merely to the surface of the samples. This clearly indicates that oxidative degradation produced by xenon exposure of samples is very high compared to the oxidative degradation observed in vermicomposted samples.

To sum up, after the study of tensile, FTIR and SEM data of nonwovens, it can be inferred that slight degradation has occurred in the samples. The nature of this degradation seems to be predominantly physical rather than a biochemical one. This is indicated by reduction in peak loads but only a slight increase in carbonyl and hydroxyl indices. Also considering the short duration of the testing, biochemical degradation could have been evidenced had the duration of composting been longer.

3.2.5. CHARACTERIZATION OF PP SPUNBOND NONWOVENS WITH ADDITIVES AFTER SOIL BURIAL

The soil burial test is an outdoor experiment, and provides a realistic environment where soil humidity, temperature and type and amount of microorganisms are in less control and change with season.

The field tests burying plastic samples in soil have been widely conducted for their biodegradation because of the similarity to actual conditions of use or disposal. The biodegradation of plastics proceeds actively under different soil conditions according to their properties, because the microorganisms responsible for the degradation differ from each other and they have their own optimal growth conditions in the soil. The biodegradability of plastics is desirable to be estimated in natural environment, where the wasted plastics are exposed as such [44].

Hence in order to study the degradation of PP spunbond nonwovens with additives under natural conditions, soil burial tests were carried out over a period of 6 months from August 2009 to February 2010. This was done in order to compare the degradation of polypropylene under natural conditions with xenon exposed samples. The samples were analyzed for their tensile properties, FTIR and SEM.

3.2.5.1. Tensile testing of PP Nonwovens with TDPA and ECM additives after 12 weeks of soil burial

In most applications envisaged for films or fibers in contact with the soil, loss in tensile properties is the most relevant practical criterion to determine its degradation [97].

Figure 3.33 shows the peak load values for PP samples after 12 weeks of soil burial.

It was observed that in general, all the samples showed a reduction in peak load after soil burial.

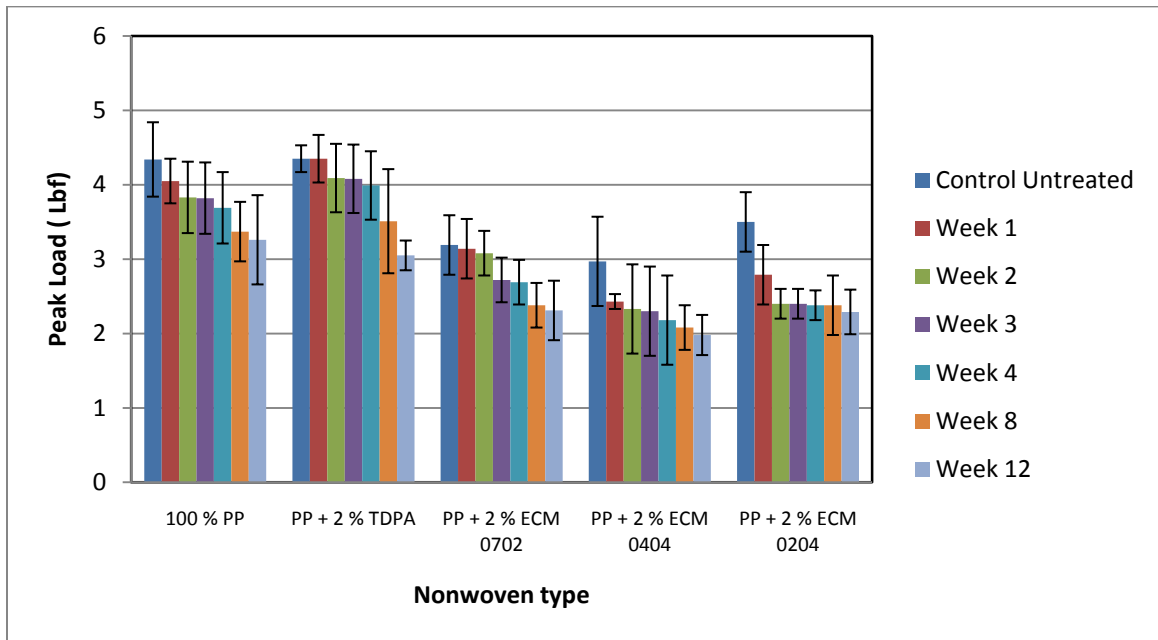


Figure 3.33. Peak load in cross direction of PP nonwovens with 2 % TDPA and ECM additives after 12 week soil burial.

The decrease in strength in 100 % control polypropylene is pronounced, with almost a 25 % reduction in peak load values after a 12 week soil burial. TDPA additive containing samples showed a reduction of 29% in peak load whereas ECM 0702, ECM 0404 and ECM 0204 additive containing samples showed a 27, 33 and 34% reduction in tensile strength. However, as compared to xenon exposure, this decrease in strength in tensile properties is not very prominent. UV plays an important role in the photo initiation of

oxidation of involving the beta scission of the backbone chain of polypropylene. In case of soil burial, the samples were buried in a pit 5 inches deep with no UV exposure. Moreover, the temperature during the last few months of December, February and January was approximately 43⁰F (6⁰C approximately). This is not enough to initiate the thermal oxidation of polypropylene. This may explain the trend of lower reduction in tensile strength during the last few months of soil burial. In absence of both UV as well as high temperatures, which act as precursors to the oxidation of polypropylene, the drop in tensile strength in samples after soil burial is not very significant. It can be inferred hence, that the reduction of peak load in the samples after soil burial is more due to physical degradation rather than a biochemical one. To verify the occurrence of chemical degradation in the samples after soil burial, FTIR of the samples was conducted.

3.2.5.2. FTIR of PP Nonwovens with TDPA and ECM additives after 12 Weeks of Soil Burial

The chemical changes of plastic films during experiments were evaluated by changes in the infrared spectra of the spunbond nonwovens. Figure 3.34 shows the IR spectrum obtained after 12 weeks of soil burial.

After a period of 12 weeks of soil burial, there were slight changes in absorption observed in the carbonyl absorption band 1610 to 1850 cm⁻¹, indicating various types of oxidation products formed during the degradation of polypropylene. Hence, carbonyl index was calculated as a ratio of absorbance at 1610 cm⁻¹ (corresponding to the carbonyl peak) to the absorbance at 2920 cm⁻¹ (corresponding to the C-H peak) . Hydroxyl index was calculated as a ratio of absorbance at 3340 cm⁻¹ (corresponding to the carbonyl peak)

to the absorbance at 2920 cm^{-1} . Figures 3.35 and 3.36 show the changes in carbonyl index and hydroxyl index respectively observed after 12 weeks of soil burial.

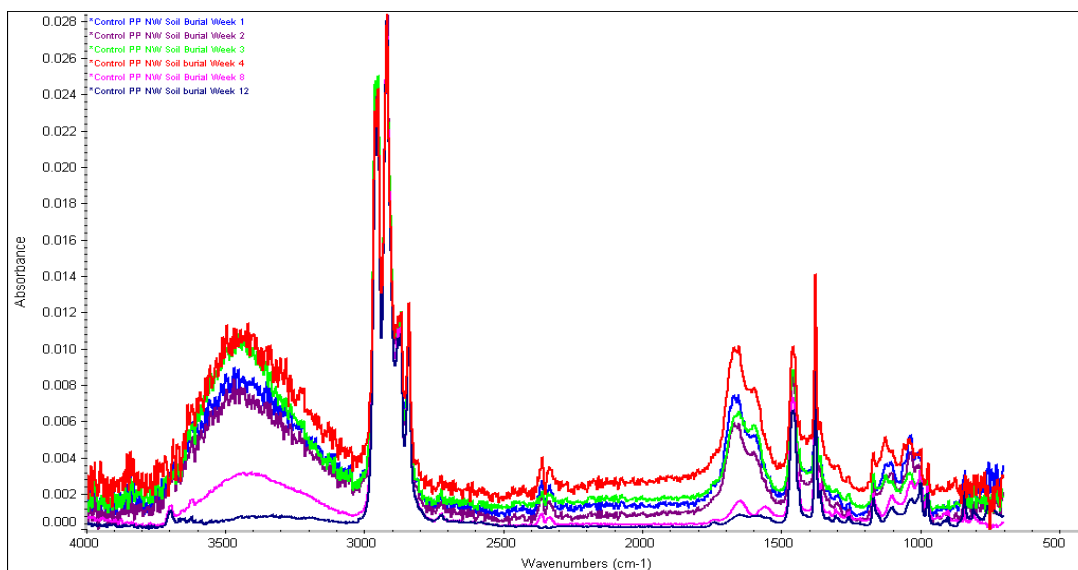


Figure 3.34. FTIR spectrum of 100 % PP nonwovens after 12 weeks of soil burial.

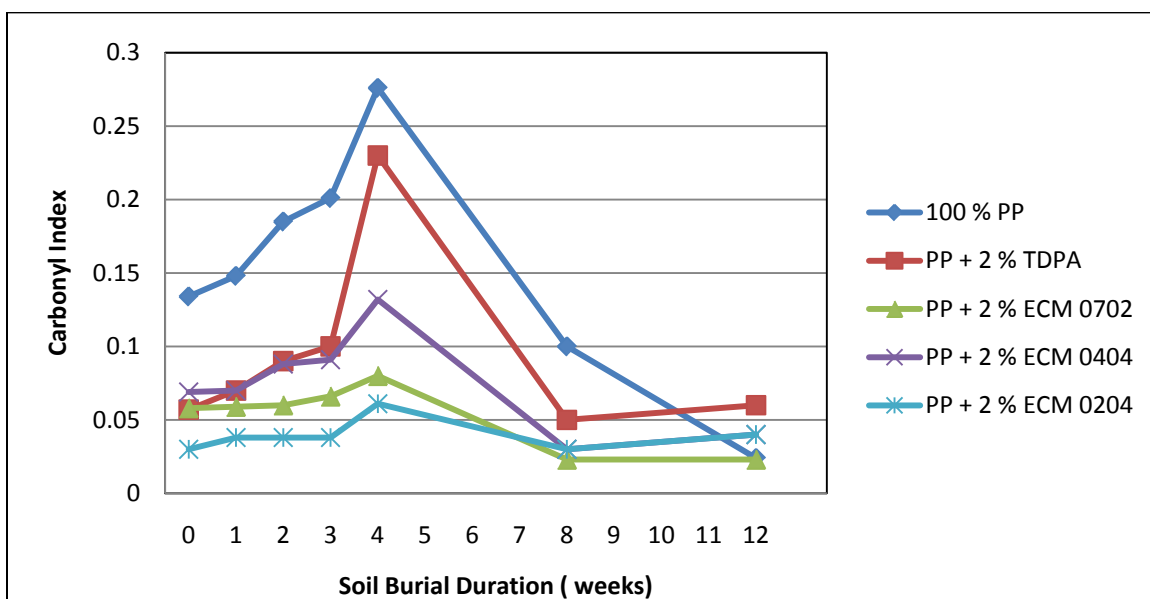


Figure 3.35. Carbonyl index for TDPA and ECM additive containing nonwovens after 12 weeks of soil burial.

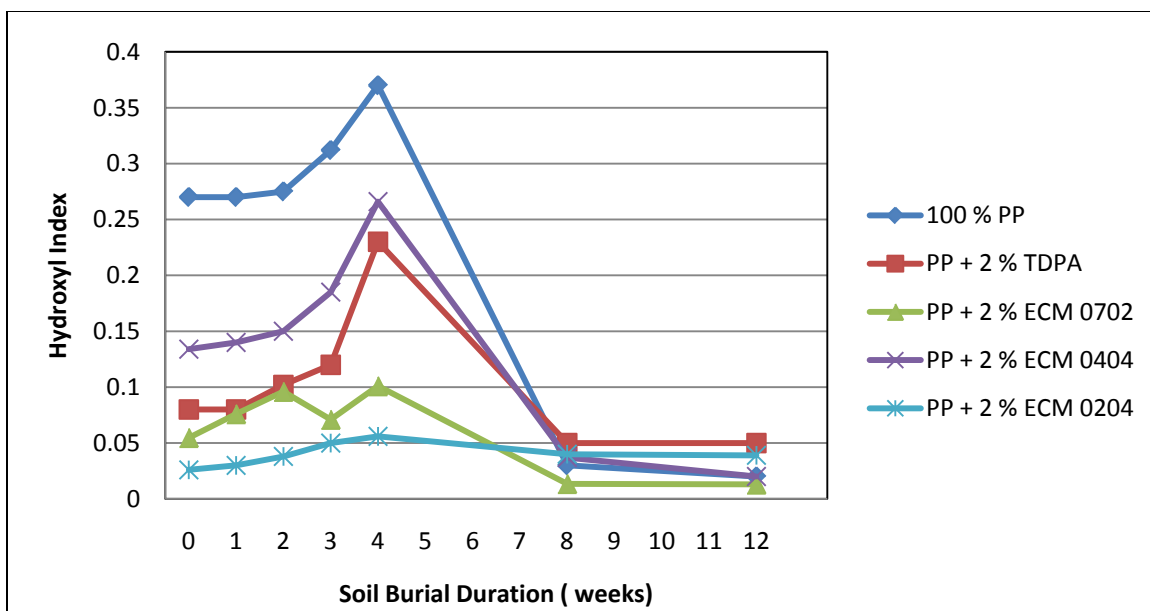


Figure 3.36. Hydroxyl index for TDPA and ECM additive containing nonwovens after 12 weeks of soil burial.

In all the samples, an increase in carbonyl index was observed after 4 weeks of soil burial. However after 8 weeks, few of the samples showed a decrease in carbonyl index as well as hydroxyl index. Similar results have been obtained by Albertsson et al. in his studies related to polyethylene biodegradation [98]. i.e. the amount of carbonyl groups decreased with prolonged exposure to a biotic environment. This has been attributed to the biotic degradation of polyolefins which is fundamentally different from abiotic degradation.

In abiotic degradation of polyolefins, oxidation occurs as a result of abiotic factors like UV exposure (photooxidation) which results in the formation of carbonyl containing

compounds like carboxylic acids, esters etc as indicated by the Norrish I, II mechanisms..

This is responsible for the consistent increase in the carbonyl index

However, the biotic degradation of polyolefins is slightly different. Albertsson et al. explains this in his study dealing with the mechanism of polyethylene biodegradation [98]. As shown in Figure 3.37, at the beginning, the main agents seem to be UV light and/or oxidizing agents, but when carbonyl groups have been produced, these are attacked by microorganisms which degrade the shorter fragments of polyethylene chains to the end products, carbon dioxide and water [98]. The alkane chain is oxidized to a carboxylic acid and the resultant acid undergoes beta-oxidation which, by reaction with coenzyme A, removes two carbon fragments from the carboxylic molecule. The two carbon fragments, acetyl-S-CoA, enter the citric acid cycle, from which carbon dioxide and water are released. In the studies conducted by Albertsson et al. a parabolic relationship was also obtained when the carbonyl index was plotted as a function of the percentage by weight of polyethylene converted to carbon dioxide. The carbonyl index increased up to 0.3 and then decreased with increasing degradation. The samples stored in air increased their carbonyl index with time, but all samples in contact with soil showed a decrease of carbonyl index with time [98].

Thus this decrease in carbonyl index maybe due to the attack of carbonyl groups by microorganisms, which degrade the polypropylene chains to carbon dioxide and water which is strongly indicative of biodegradation of polypropylene.

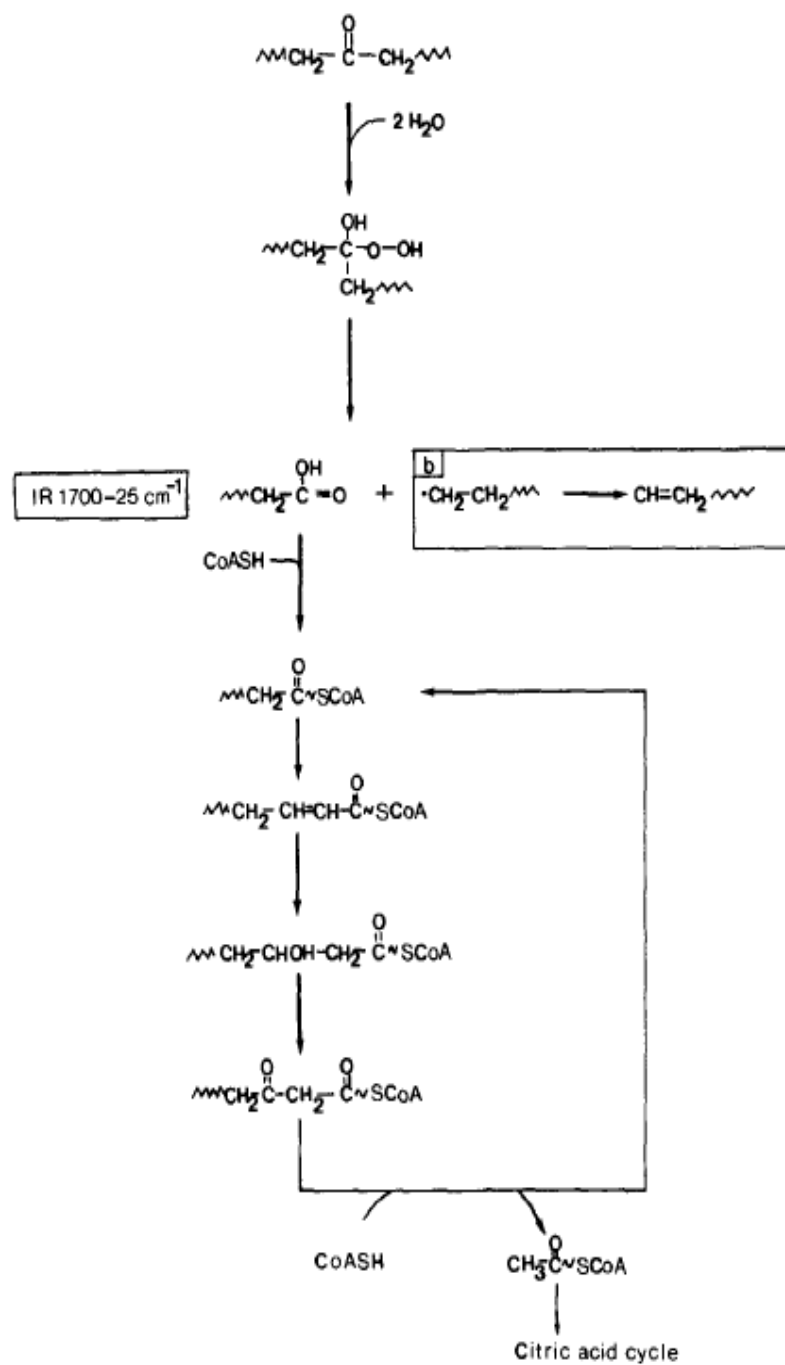


Figure 3.37. Proposed mechanism for the biodegradation of polyethylene [98].

3.2.5.3. SEM of PP Nonwovens with TDPA and ECM additives after 12 week Soil Burial

SEM analysis of the nonwovens after 12 weeks of soil burial was done in order to study the changes in morphology which may have occurred due to degradation. Figure 3.38 (d) shows the effect of 12 weeks of soil burial on the nonwoven

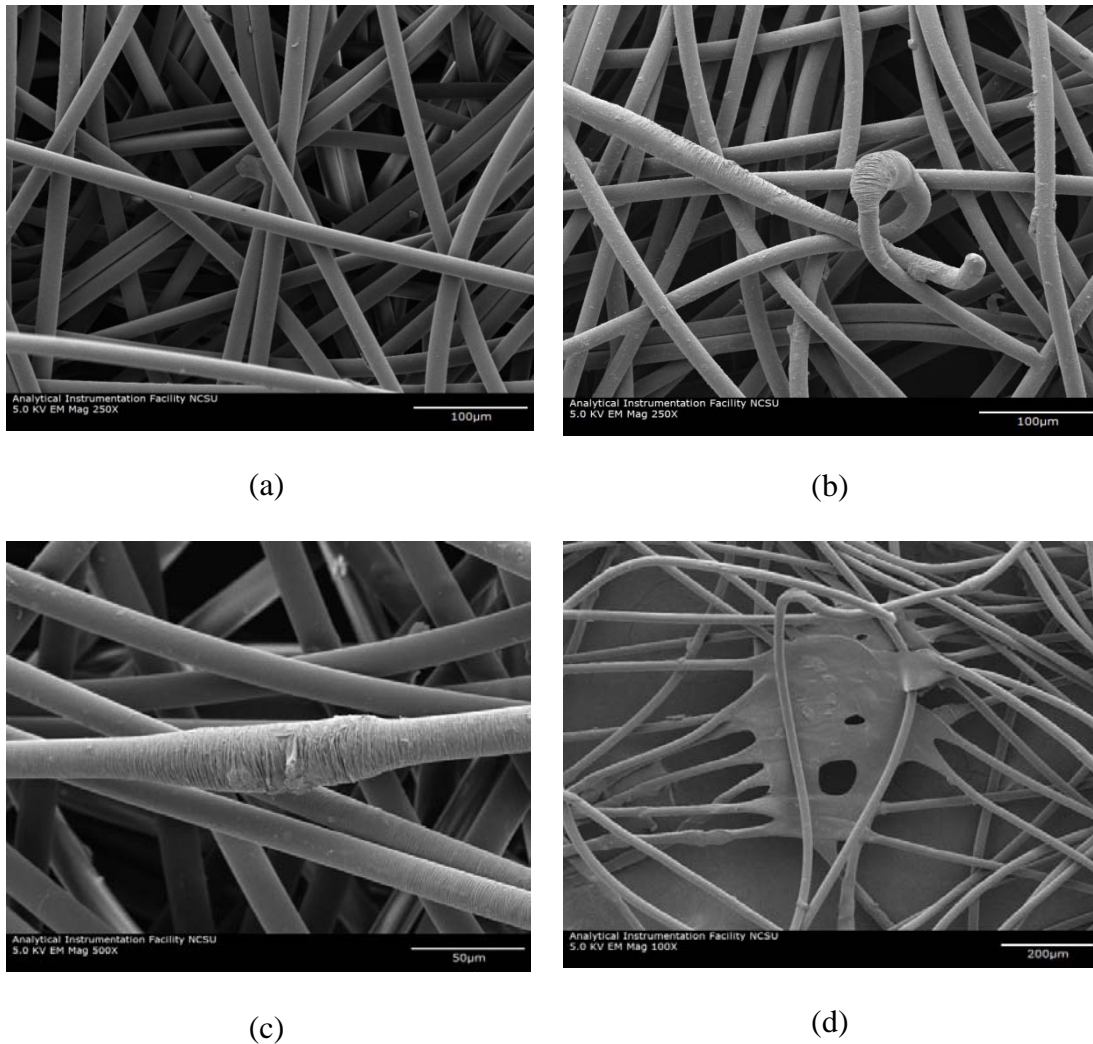


Figure 3.38. SEM micrographs of (a) Control 100 % PP nonwoven, (b) 100 % PP nonwovens after 8 weeks of soil burial, (c) 100 % PP nonwoven after 12 weeks of soil burial (d) Bond points in 100 % PP nonwoven after 12 weeks of soil burial.

A notable tearing of bond points was observed in most samples. This may have caused the decrease in tensile strength of most samples. Some of the samples showed filaments tearing out of the bond points, and cracked fibers. In some cases, as shown in Figure 3.38(b) and 3.38 (c), swelling of fibers was also observed. However, morphologically, there does not seem to be a significant deterioration as compared to UV treated samples which fell apart after xenon exposure. This also explains the slight reduction in peak load observed in soil buried samples as compared to the catastrophic drop in tensile strength which was observed in xenon exposed samples. However, as shown in the FTIR analysis, there is evidence of bio-chemical degradation marked by the initial increase and subsequent decrease in carbonyl index. These are clearly indicative of degradation of samples occurring under biotic conditions.

Thus to sum up, it can be inferred that though nonwoven samples buried in soil did not show significant physiological degradation, there is definite indication of bio-chemical degradation having occurred.

SECTION 4- CONCLUSIONS

Increasing concerns of plastic accumulation in the environments have led to larger demands for degradable plastics which offer suitable properties during their shelf life but can decompose readily on disposal. The present study was conducted to study the degradation mechanisms of polypropylene and develop an effective prodegradant additive system which could further this cause. Accordingly polypropylene filaments and nonwovens were developed using prodegradant additives and analyzed for their degradability.

From the current study, it can be inferred that degradation of polypropylene filaments and nonwovens with additives depends on various factors like the amount of the additive used, type and nature of degradation carried out (abiotic or biotic) etc.

More specifically, the following conclusions were drawn from the experimental results:

There are two types of degradation possible in polypropylene, namely abiotic degradation and biotic degradation. These are fundamentally different in their degradation mechanisms.

In abiotic degradation of polyolefins, oxidation occurs as a result of abiotic factors like UV exposure (photooxidation) which results in the formation of carbonyl containing compounds like carboxylic acids, esters etc as indicated by the Norrish I, II mechanisms.

Pro-oxidants, also known as pro-degradants like the ones used in the present study clearly have a major role to play in the abiotic degradation of polypropylene. These functional groups act as initiators of thermal and photooxidation of the hydrocarbon polymer chains. These abiotic degradation processes result in functional macromolecules, which thermally and/or photochemically cleave repeatedly to low molecular weight fragments, especially in the presence of transition metal ions. This has been illustrated by the following

- Catastrophic reduction in tensile properties (elongation and tenacity) in pro-degradant additive containing samples was observed after 180 hour xenon arc lamp exposure. The samples became brittle on xenon exposure which was proved by an increase in tensile modulus. The effect of oxidative degradation was more pronounced in additive containing samples as compared to 100 % PP control samples. Among TDPA and ECM additives, TDPA was proved to be a better pro-degradant because TDPA containing samples showed a substantial decrease in elongation and tenacity, even when used in lesser concentrations (1%).
- FTIR studies showed an increase in both carbonyl and hydroxyl index in xenon exposed samples containing additives as compared to 100 % PP samples. This confirms the occurrence of chemical degradation marked by the formation of carboxylic acid, esters which help to initiate degradation of PP
- SEM studies clearly indicate the breakdown of fibers and nonwovens on xenon arc lamp exposure. However, this decrease is more prominent in pro-degradant

additive containing samples. Images clearly indicate that the extent of degradation observed is more prominent in TDPA than in ECM additive containing samples, evidenced by extensive cracks in the fiber cross section as well as presence of chopped fibers in UV exposed samples.

In the present study, biotic degradation was studied by vermicomposting and soil burial methods. The following conclusions can be made from these studies

- Tensile studies do indicate a significant drop in peak load after vermicomposting and soil burial. However, it is not as significant as the tensile strength reduction occurring in xenon exposed samples. SEM analyses of the samples also support this.
- FTIR analysis showed an initial increase in carbonyl index and hydroxyl index followed by a drastic reduction in these indices after 8 weeks of soil burial. This decrease may have occurred due to the microbial degradation of polypropylene into smaller chain fragments which result in the formation of carbon dioxide and water. This is strongly indicative of the occurrence of bio-chemical degradation of PP.

It was observed that the presence of these prodegradant additives did not have a major effect on the bio-chemical degradation of polypropylene.

In a nutshell, the study illustrates the role of additives in the abiotic degradation of polypropylene fibers and nonwovens. It has been clearly shown that degradation of polypropylene nonwovens can be controlled by usage of these pro-degradant additives. Photo degradation was observed to have caused maximum degradation in PP samples as compared to other biotic methods like vermicomposting and soil burial. This photo degradation was more pronounced in pro-degradaant additive containing samples. However, biodegradation of these plastics cannot be attributed to a single cause, but is a combined effect of both abiotic and biotic factors. In practice, biodegradation cannot be separated from abiotic degradation and involves a combined effect of UV, temperature, water and microorganisms.

SECTION 5 - RECOMMENDATIONS FOR FUTURE WORK

The present study dealt with the degradation of polypropylene fibers and nonwovens after abiotic degradation like xenon arc lamp exposure and biotic degradation like soil burial and vermicomposting. The synergy between biotic and abiotic methods could be further studied by pretreatment of these PP nonwovens by xenon exposure and then disposing them to the biotic environment.

Chemiluminescence (CL) could be used to study the degradation mechanisms in detail. This technique has become a useful technique for the study of polymer degradation, oxidation mechanisms and kinetics, as well as stabilizer efficiency. The chemiluminescence in polymers is due to the light emission that accompanies the thermal decomposition of the thermooxidative degradation products (hydroperoxides), which are formed during processing or service life of the material under ambient conditions. This technique can be useful in quantifying the extent of degradation occurring in these polypropylene nonwovens.

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APPENDIX

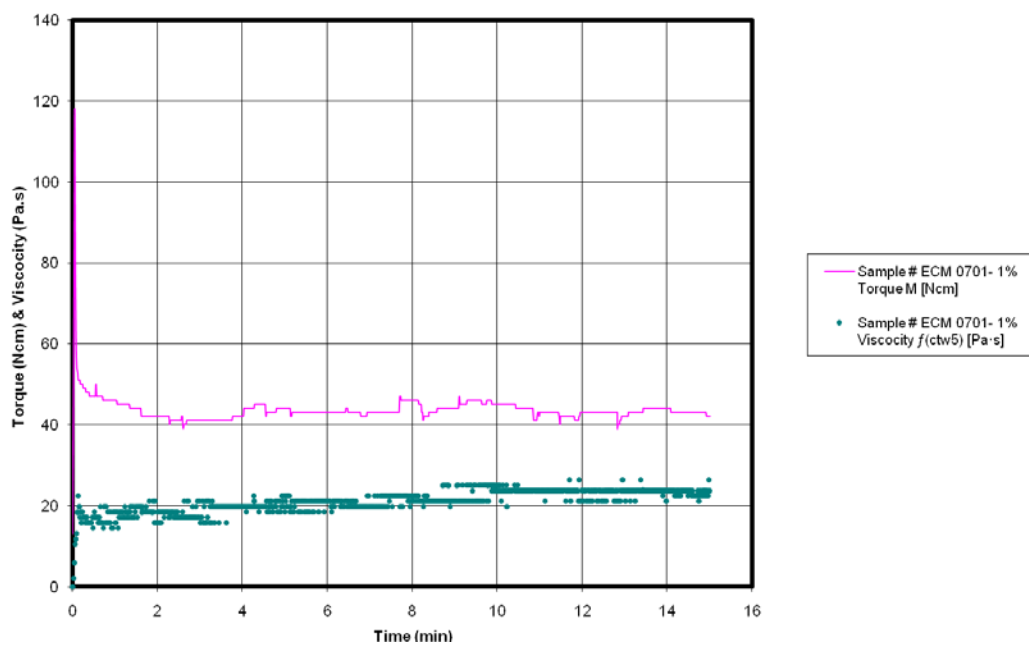


Figure A.1. Torque and viscosity measurements for polypropylene with 1 % ECM 0701.

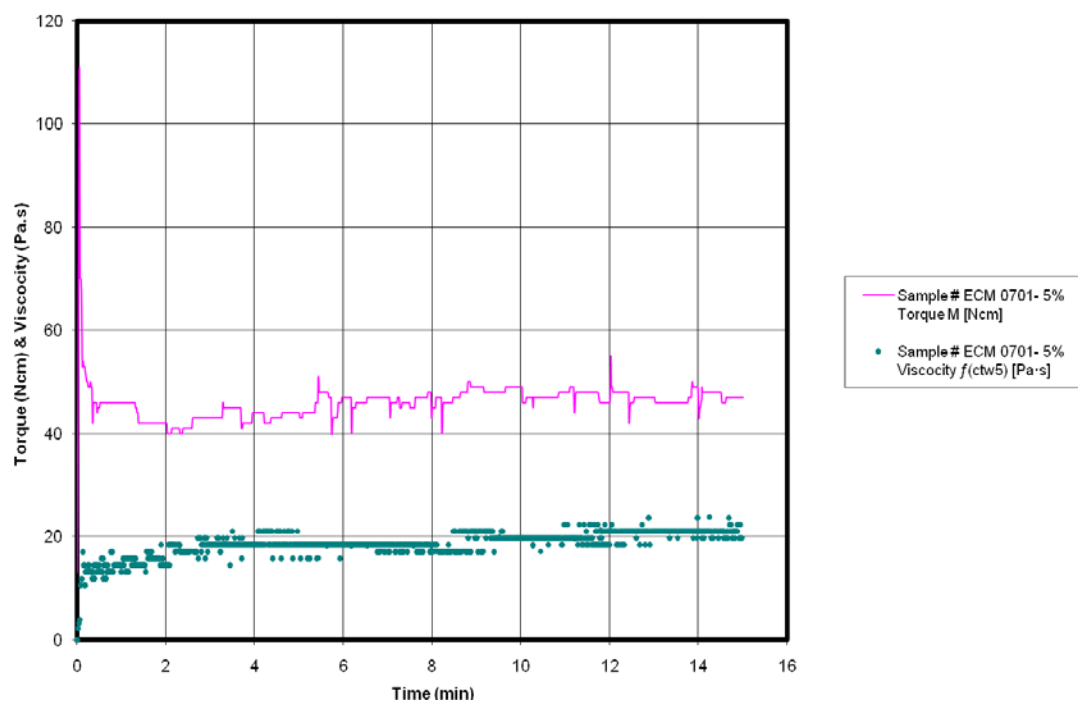


Figure A.2. Torque and viscosity measurements for polypropylene with 5 % ECM 0701.

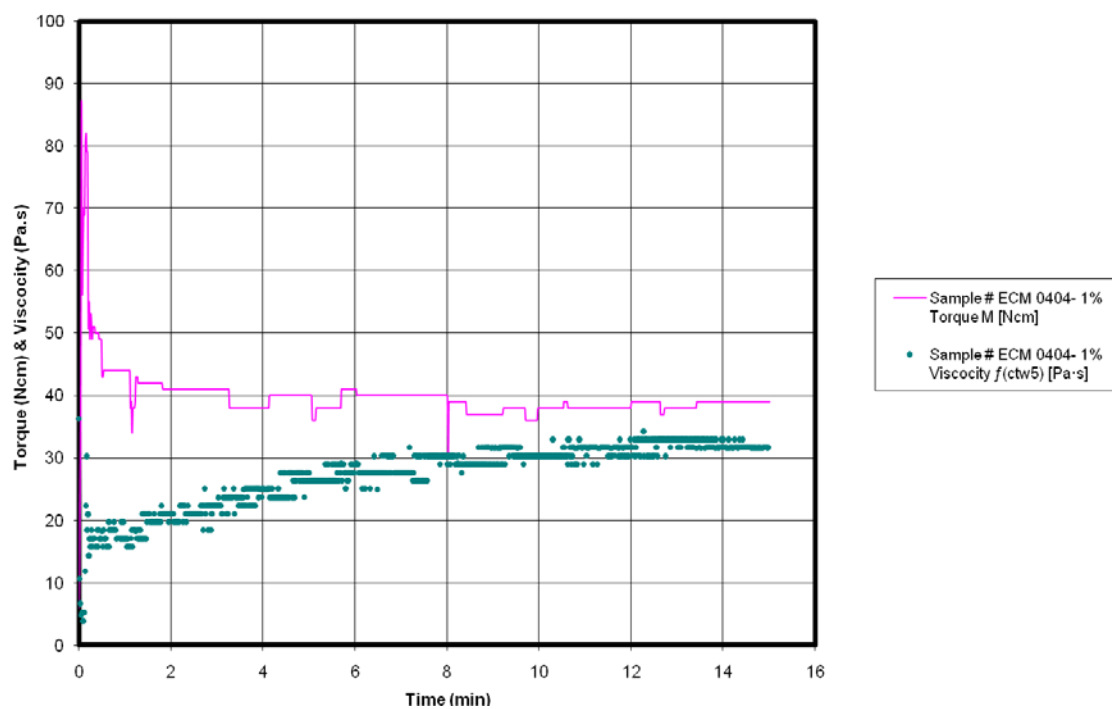


Figure A.3. Torque and viscosity measurements for polypropylene with 1 % ECM 0404.

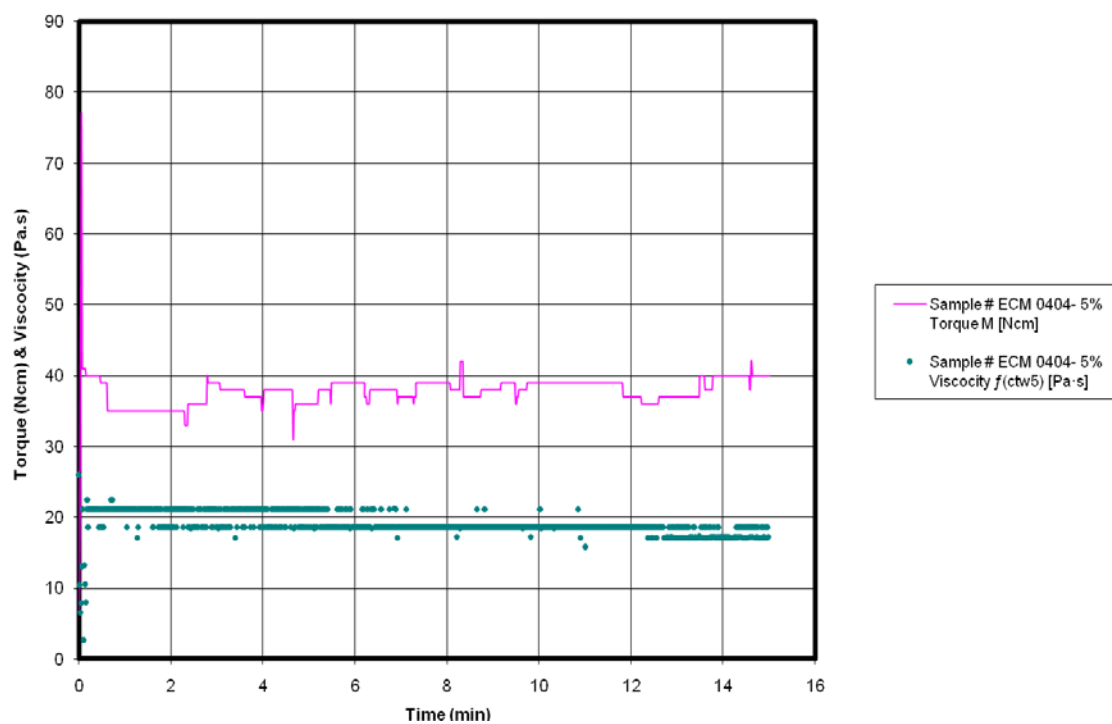


Figure A.4. Torque and viscosity measurements for polypropylene with 5 % ECM 0404.

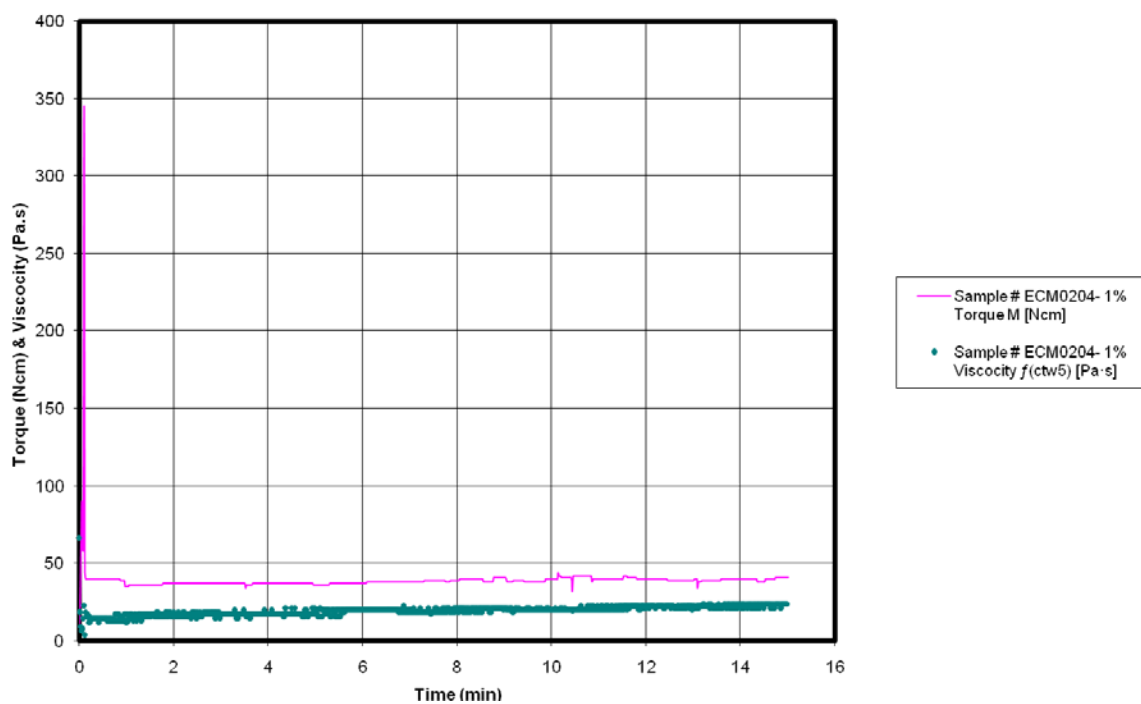


Figure A.5. Torque and viscosity measurements for polypropylene with 1 % ECM 0204.

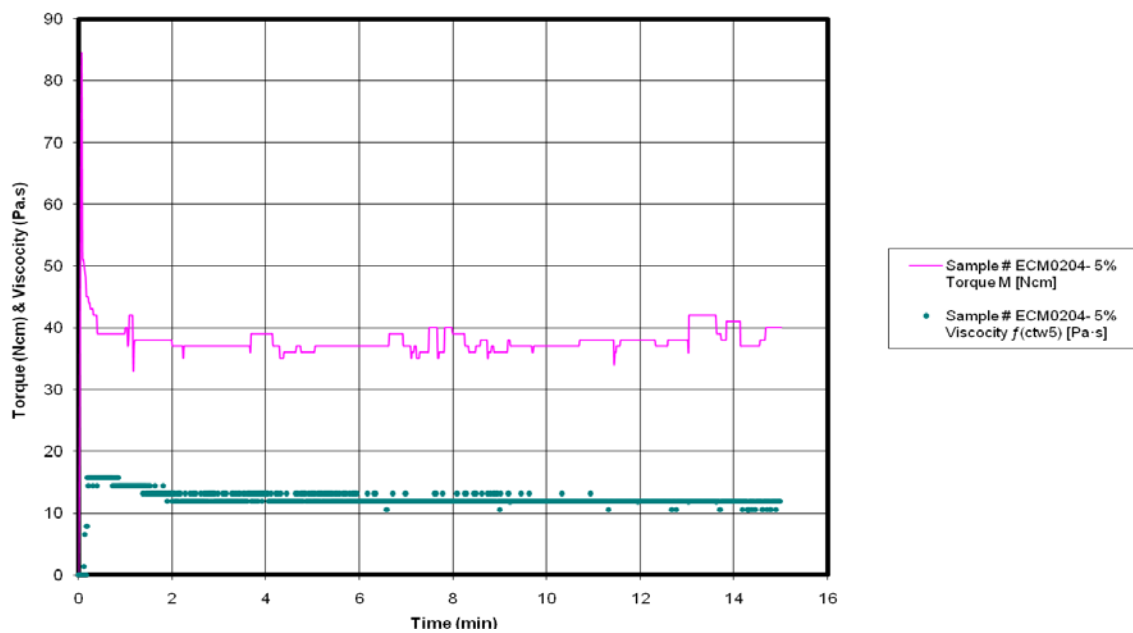


Figure A.6. Torque and viscosity measurements for polypropylene with 5 % ECM 0204.

Table A.1. Elongation at peak load of PP Filaments with 1% and 2 % TDPA and ECM additives after 0, 80, 180 hour xenon exposure.

Elongation at peak load (%)							
Filament Sample	Denier	original		After 80 hour. exposure		After 180 hour. exposure	
		Mean	Std Dev	Mean	Std Dev	Mean	Std Dev
100 % PP	659.2	301.95	18.53	297.51	14.03	3.76	1.48
PP + TDPA (1 %)	659.2	277.15	22.17	134.85	11.4	0.97	0.29
PP + TDPA (2 %)	659.2	272.59	14.67	182.36	48	0.96	0.18
PP + ECM 0701 (1%)	654	226	13	185	17	38.2	2.0
PP + ECM 0701 (2 %)	654	240	11	231	15	3.5	1.0
PP + ECM 0702 (1 %)	654	280.3	11.9	248.3	9	2.74	0.87
PP + ECM 0702 (2 %)	654	231	11.2	185	8.2	2.44	1.0
PP + ECM 0204 (1 %)	654	264.6	9.0	225.1	8.0	4.05	1.4
PP + ECM 0204 (2%)	654	259.6	13.0	248	10	6.9	3.5

Table A.2. Tenacity of PP Filaments with 1% and 2 % TDPA and ECM additives after 0,80, 180 hour xenon exposure.

Tenacity (gf/denier)							
Filament Sample	Denier	original		After 80 hour. exposure		After 180 hour. exposure	
		Mean	Std Dev	Mean	Std Dev	Mean	Std Dev
100 % PP	659.2	1.32	0.07	1.23	0.1	0.43	0.2
PP + TDPA (1 %)	659.2	1.21	0.10	0.42	0.21	0.11	0.06
PP + TDPA (2 %)	659.2	1.25	0.06	0.77	0.29	0.14	0.06
PP + ECM 0701 (1 %)	654	0.92	0.10	0.45	0.12	0.30	0.07
PP + ECM 0701 (2 %)	654	1.05	0.05	0.96	0.07	0.26	0.04
PP + ECM 0702 (1 %)	654	1.17	0.03	0.99	0.07	0.25	0.06
PP + ECM 0702 (2 %)	654	1.04	0.05	0.80	0.03	0.23	0.06
PP + ECM 0204 (1 %)	654	1.17	0.06	0.94	0.03	0.24	0.06
PP + ECM 0204 (2%)	654	1.17	0.06	1.10	0.04	0.30	0.06

Table A.3. Modulus of PP Filaments with 1% and 2 % TDPA and ECM additives after 0,80, 180 hour xenon exposure.

Modulus at peak load (%)							
Filament Sample	Denier	Original		After 80 hour. exposure		After 180 hour. exposure	
		Mean	Std Dev	Mean	Std Dev	Mean	Std Dev
100 % PP	659.2	6.27	1.0	6.28	1.1	10.45	1.48
PP + TDPA (1 %)	659.2	8.32	0.83	11.0	0.6	14.3	2.6
PP + TDPA (2 %)	659.2	10.09	0.8	10.1	0.8	14.3	1.1
PP + ECM 0701 (1 %)	654	9.09	1.0	9.7	1.9	13.91	2.4
PP + ECM 0701 (2 %)	654	9.37	0.65	9.9	0.6	16.00	1.1
PP + ECM 0702 (1 %)	654	9.2	0.24	9.2	0.28	14.24	1.2
PP + ECM 0702 (2 %)	654	10.05	0.68	10.2	1.2	15.00	1.6
PP + ECM 0204 (1 %)	654	10.6	1.7	8.9	0.94	11.74	2.3
PP + ECM 0204 (2%)	654	9.0	1.2	9.1	1.3	12.11	1.2

Table A.4. Carbonyl index and hydroxyl index for PP filaments with TDPA and ECM additives after 0, 80 and 180 hours of xenon exposure.

Filament Sample	Carbonyl (1610 cm ⁻¹) A*	C H (2920 cm ⁻¹) B*	Hydroxyl (3340 cm ⁻¹) C*	Carbonyl index	Hydroxyl index
100 % PP unexposed	0.0017	0.058	0.0013	0.029	0.022
100 % PP 80 hour exposure	0.0024	0.044	0.0048	0.054	0.109
100 % PP 180 hour exposure	0.0049	0.515	0.0061	0.096	0.118
PP + 1% TDPA unexposed	0.0041	0.065	0.004	0.063	0.067
PP + 1% TDPA 80 hour exposure	0.0028	0.0431	0.0047	0.066	0.109
PP + 1% TDPA 80 hour exposure	0.0022	0.022	0.00265	0.097	0.115
PP + 2% TDPA unexposed	0.00147	0.0676	0.0028	0.023	0.040
PP + 2% TDPA 80 hour exposure	0.00317	0.0483	0.0046	0.065	0.095
PP + 2% TDPA 80 hour exposure	0.00372	0.0527	0.0054	0.071	0.10
PP + 1% ECM 0702 unexposed	0.0019	0.058	0.0022	0.033	0.037
PP + 1 % ECM 0702 80 hour exposure	0.00363	0.0720	0.0044	0.050	0.06
PP + 1 % ECM 0702 80 hour exposure	0.00370	0.0434	0.0045	0.08	0.103
PP + 2% ECM 0702 unexposed	0.0024	0.087	0.0023	0.027	0.026
PP + 2 % ECM 0702 80 hour exposure	.00234	0.0809	0.00222	0.028	0.027
PP + 2 % ECM 0702 80 hour exposure	.00216	0.039	0.00179	0.054	0.045
PP + 1% ECM 0701 unexposed	0.00217	0.0464	0.00188	0.046	0.0405
PP + 1 % ECM 0701 80 hour exposure	0.0018	0.0257	0.0009	0.070	0.0475
PP + 1% ECM 0701 80 hour exposure	0.0051	0.0383	0.0042	0.133	0.10
PP + 2% ECM 0701 unexposed	0.0041	0.0732	0.0102	0.056	0.139
PP + 2% ECM 0701 80 hour exposure	0.0058	0.0793	0.0054	0.0731	0.068
PP + 2% ECM 0701 180 hour exposure	0.0044	0.0535	0.0039	0.088	0.072
PP + 1% ECM 0204 unexposed	0.00206	0.0515	0.00229	0.04	0.044
PP + 1 % ECM 0204 80 hour exposure	0.0017	0.0403	0.0022	0.04	0.055
PP + 1% ECM 0204 180 hour exposure	0.0035	0.0829	0.0060	0.042	0.072
PP + 2% ECM 0204 unexposed	0.0017	0.0445	0.0022	0.038	0.049
PP + 2 % ECM 0204 80 hour exposure	0.0032	0.0583	0.0034	0.054	0.0583
PP + 2% ECM 0204 80 hour exposure	0.0029	0.0404	0.0061	0.066	0.1509

A*, B* , C* indicate the absorbencies at 1610, 2920 and 3340 cm⁻¹ respectively

Table A.5. Elongation at peak load of PP nonwovens with 2 % TDPA and ECM additives after 0, 80, 180 hour xenon exposure.

Elongation at peak load (%)						
Nonwoven Sample	Original		After 80 hour. exposure		After 180 hour. exposure	
	Mean	Std Dev.	Mean	Std Dev.	Mean	Std Dev.
100 % PP	52.1	2.3	53.7	4	40	7
PP + TDPA (2 %)	64	8	8.7	2	*	*
PP + ECM 0701 (2 %)	45	7	29	5	*	*
PP + ECM 0702 (2 %)	11.66	1	11.63	1	4.7	1.7
PP + ECM 0204 (2%)	13.06	1	7.3	2	1.7	0.7

*Samples were too weak to be tested on Instron.

Table A.6. Peak load values of PP nonwovens with 2 % TDPA and ECM additives after 0, 80, 180 hour xenon exposure.

Peak load (lbf)						
Nonwoven Sample	Original		After 80 hour. exposure		After 180 hour. exposure	
	Mean	Std Dev.	Mean	Std Dev.	Mean	Std Dev.
100 % PP	8.46	0.9	8.08	1	6.18	1
PP + TDPA (2 %)	8.96	0.6	2.51	0.6	*	*
PP + ECM 0701 (2 %)	6.2	0.7	5.13	0.7	*	*
PP + ECM 0702 (2 %)	5	0.5	4.4	1	2.69	0.8
PP + ECM 0204 (2%)	5.97	0.4	4.03	0.7	1.14	0.9

Table A.7. Carbonyl index and Hydroxyl index for PP nonwovens with TDPA and ECM additives after 0, 80 and 180 hours of xenon exposure.

Nonwoven Sample	Carbonyl (1610 cm ⁻¹) A*	C H (2920 cm ⁻¹) B*	Hydroxyl (3340 cm ⁻¹) C*	Carbonyl index	Hydroxyl index
100 % PP unexposed	0.005	0.037	0.0104	0.135	0.27
100 % PP 80 hour exposure	0.009	0.037	0.0137	0.237	0.36
100 % PP 180 hour exposure	0.010	0.036	0.0147	0.273	0.39
PP + 2% TDPA unexposed	0.0023	0.0404	0.0040	0.056	0.099
PP + 2% TDPA 80 hour exposure	0.0037	0.0349	0.0071	0.106	0.203
PP + 2% TDPA 80 hour exposure	0.0087	0.048	0.0140	0.181	0.291
PP + 2% ECM 0702 unexposed	0.0031	0.0418	0.0039	0.07	0.09
PP + 2 % ECM 0702 80 hour exposure	0.0024	0.0275	0.0041	0.08	0.15
PP + 2 % ECM 0702 80 hour exposure	0.0066	0.0285	0.0108	0.23	0.38
PP + 2% ECM 0404 unexposed	0.0041	0.0732	0.0102	0.056	0.03
PP + 2% ECM 0404 80 hour exposure	0.0058	0.0793	0.0054	0.0731	0.09
PP + 2% ECM 0404 180 hour exposure	0.0044	0.0535	0.0039	0.088	0.153
PP + 2% ECM 0204 unexposed	0.0017	0.0445	0.0022	0.038	0.02
PP + 2 % ECM 0204 80 hour exposure	0.0032	0.0583	0.0034	0.054	0.14
PP + 2% ECM 0204 80 hour exposure	0.0029	0.0404	0.0061	0.066	0.25

A*, B* , C* indicate the absorbencies at 1610, 2920 and 3340 cm⁻¹respectively

Table A.8. Peak load values of PP nonwovens with 2 % TDPA and ECM additives after 4 week vermicomposting.

Peak load (lbf)										
Nonwoven Sample	Control Untreated		Week 1		Week 2		Week 3		Week 4	
	Mean	Std Dev.	Mean	Std Dev.	Mean	Std Dev.	Mean	Std Dev.	Mean	Std Dev.
100 % PP	4.63	0.5	4.58	0.3	4.24	0.86	4.02	0.48	3.82	0.78
PP + 2 % TDPA	4.79	0.18	4.44	0.32	4.08	0.42	4.05	0.46	3.95	0.5
PP + 2 % ECM 0702	3.19	0.4	2.84	0.4	2.76	0.3	2.44	0.3	2.3	0.5
PP + 2 % ECM 0404	2.85	0.6	2.76	0.1	2.64	0.3	2.48	0.6	2.32	0.4
PP + 2 % ECM 0204	3.5	0.4	2.79	0.4	2.4	0.4	2.4	0.2	2.17	0.3

Table A.9. Carbonyl index and hydroxyl index for PP nonwovens with TDPA and ECM additives after 4 week vermicomposting.

Nonwoven sample	Carbonyl (1610 cm^{-1}) A*	C H (2920 cm^{-1}) B*	Hydroxyl (3340 cm^{-1}) C*	Carbonyl index	Hydroxyl index
100 % PP unexposed	0.005	0.037	0.0104	0.042	0.2
100 % PP Week 1	0.0046	0.0474	0.0058	0.095	0.22
100 % PP Week 2	0.0035	0.0346	0.0077	0.101	0.22
100 % PP Week 3	0.0057	0.0360	0.0085	0.158	0.23
100 % PP Week 4	0.0032	0.0281	0.0046	0.167	0.26
PP + 2% TDPA unexposed	0.00256	0.0447	0.0051	0.057	0.11
PP + 2% TDPA Week 1	0.0025	0.0372	0.0041	0.067	0.11
PP + 2% TDPA Week 2	0.00267	0.0374	0.0030	0.071	0.11
PP + 2% TDPA Week 3	0.00379	0.0333	0.0042	0.111	0.12
PP + 2% TDPA Week 4	0.00251	0.0195	0.0029	0.129	0.15
PP + 2% ECM 0702 unexposed	0.00348	0.048	0.0047	0.072	0.097
PP + 2 % ECM 0702 Week 1	0.0035	0.037	0.007	0.09	0.188
PP + 2 % ECM 0702 Week 2	0.0036	0.034	0.0069	0.10	0.199
PP + 2 % ECM 0702 Week 3	0.00353	0.028	0.0068	0.125	0.242
PP + 2 % ECM 0702 Week 4	0.0045	0.025	0.0085	0.170	0.33
PP + 2% ECM 0404 unexposed	0.00249	0.0483	0.0048	0.06	0.03
PP + 2 % ECM 0404 Week 1	0.0037	0.0447	0.0033	0.08	0.075
PP + 2 % ECM 0404 Week 2	0.0037	0.0465	0.0040	0.081	0.08
PP + 2 % ECM 0404 Week 3	0.0048	0.0457	0.0061	0.122	0.135
PP + 2 % ECM 0404 Week 4	0.00396	0.0246	0.0038	0.16	0.15
PP + 2% ECM 0204 unexposed	0.0025	0.0820	0.00218	0.03	0.03
PP + 2 % ECM 0204 Week 1	0.0025	0.082	0.0021	0.030	0.02
PP + 2 % ECM 0204 Week 2	0.0017	0.045	0.00169	0.04	0.037
PP + 2 % ECM 0204 Week 3	0.0018	0.036	0.00149	0.049	0.04
PP + 2 % ECM 0204 Week 4	0.0036	0.047	0.00236	0.076	0.06

A*, B* , C* indicate the absorbencies at 1610, 2920 and 3340 cm^{-1} respectively

Table A.10. Carbonyl index and hydroxyl index for PP nonwovens with TDPA and ECM additives after 12 week soil burial

Nonwoven Sample	Carbonyl (1610 cm ⁻¹) A*	C H (2920 cm ⁻¹) B*	Hydroxyl (3340 cm ⁻¹) C*	Carbonyl index	Hydroxyl index
100 % PP unexposed	0.0051	0.0377	0.0104	0.134	0.27
100 % PP Week 1	0.0066	0.0443	0.0106	0.148	0.27
100 % PP Week 2	0.0066	0.035	0.0098	0.185	0.275
100 % PP Week 3	0.0082	0.0406	0.0127	0.201	0.312
100 % PP Week 4	0.0077	0.0278	0.0100	0.276	0.37
100 % PP Week 8	0.00181	0.0616	0.00188	0.02	0.09
100 % PP Week 12	0.00142	0.0588	0.00158	0.02	0.02
PP + 2% TDPA unexposed	0.00233	0.0405	0.0040	0.057	0.08
PP + 2% TDPA Week 1	0.0017	0.0240	0.00202	0.07	0.08
PP + 2% TDPA Week 2	0.0040	0.0042	0.0043	0.09	0.102
PP + 2% TDPA Week 3	0.00328	0.0310	0.0040	0.1	0.12
PP + 2% TDPA Week 4	0.00361	0.0156	0.00359	0.23	0.23
PP + 2% TDPA Week 8	0.00208	0.0358	0.00196	0.05	0.05
PP + 2% TDPA Week 12	0.00195	0.0304	0.0015	0.06	0.05
PP + 2% ECM 0702 unexposed	0.00348	0.048	0.0047	0.058	0.0547
PP + 2 % ECM 0702 Week 1	0.00208	0.035	0.0024	0.059	0.076
PP + 2 % ECM 0702 Week 2	0.00187	0.0304	0.00290	0.06	0.096
PP + 2 % ECM 0702 Week 3	0.00246	0.035	0.00228	0.066	0.071
PP + 2 % ECM 0702 Week 4	0.00254	0.0314	0.00316	0.08	0.101
PP + 2 % ECM 0702 Week 8	0.0011	0.0472	0.00064	0.023	0.0135
PP + 2 % ECM 0702 Week 12	0.00108	0.0472	0.00064	0.023	0.013
PP + 2% ECM 0404 unexposed	0.00249	0.0356	0.0048	0.069	0.134
PP + 2 % ECM 0404 Week 1	0.00243	0.0306	0.0043	0.07	0.14
PP + 2 % ECM 0404 Week 2	0.0031	0.0359	0.0054	0.088	0.15
PP + 2 % ECM 0404 Week 3	0.00298	0.0314	0.00600	0.091	0.185
PP + 2 % ECM 0404 Week 4	0.00283	0.0214	0.0057	0.132	0.266
PP + 2 % ECM 0404 Week 8	0.00194	0.0457	0.00170	0.04	0.037
PP + 2 % ECM 0404 Week 12	0.00123	0.0365	0.00076	0.03	0.02
PP + 2% ECM 0204 unexposed	0.0025	0.0820	0.00218	0.03	0.026
PP + 2 % ECM 0204 Week 1	0.00285	0.0829	0.0029	0.034	0.03
PP + 2 % ECM 0204 Week 2	0.00250	0.0657	0.0025	0.038	0.038
PP + 2 % ECM 0204 Week 3	0.00291	0.0750	0.00382	0.038	0.05
PP + 2 % ECM 0204 Week 4	0.0036	0.0585	0.0033	0.061	0.056
PP + 2 % ECM 0204 Week 8	0.0021	0.0452	0.00215	0.04	0.04
PP + 2 % ECM 0204 Week 12	0.00224	0.0594	0.00237	0.037	0.039

A*, B* , C* indicate the absorbencies at 1610, 2920 and 3340 cm⁻¹respectively

Table A.11. Peak load values of PP nonwovens with 2 % TDPA and ECM additives after 12 week soil burial.

Nonwoven Sample	Peak load (lbf)									
	100 % PP		PP + 2 % TDPA		PP + 2 % ECM 0702		PP + 2 % ECM 0404		PP + 2 % ECM 0204	
	Mean	Std Dev	Mean	Std Dev	Mean	Std Dev	Mean	Std Dev	Mean	Std Dev
Control Untreated	4.34	0.5	4.35	0.18	3.19	0.4	2.97	0.6	3.5	0.4
Week 1	4.05	0.3	4.35	0.3	3.14	0.4	2.43	0.1	2.79	0.4
Week 2	3.83	0.86	4.09	0.4	3.08	0.3	2.33	0.3	2.4	0.4
Week 3	3.82	0.48	4.08	0.4	2.72	0.5	2.3	0.6	2.4	0.2
Week 4	3.69	0.78	3.99	0.5	2.69	0.5	2.18	0.4	2.38	0.3
Week 8	3.37	0.4	3.51	0.7	2.38	0.3	2.08	0.5	2.38	0.6
Week 12	3.26	0.6	3.05	0.2	2.31	0.4	1.98	0.2	2.29	0.3