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BIODEGRADATION AND PHOTODEGRADATION OF POLYLACTIC ACID AND POLYLACTIC ACID/ POLYHYDROXYALKANOATE BLENDS NONWOVEN AGRICULTURAL MULCHES IN AMBIENT SOIL CONDITIONS

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I am submitting herewith a dissertation written by Sathiskumar Dharmalingam entitled "BIODEGRADATION AND PHOTODEGRADATION OF POLYLACTIC ACID AND POLYLACTIC ACID/ POLYHYDROXYALKANOATE BLENDS NONWOVEN AGRICULTURAL MULCHES IN AMBIENT SOIL CONDITIONS." I have examined the final electronic copy of this dissertation for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, with a major in Biosystems Engineering.

Douglas G. Hayes, Major Professor

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A Dissertation Presented for the
Doctor of Philosophy
Degree
The University of Tennessee, Knoxville

Sathiskumar Dharmalingam
May 2014

DEDICATION

I dedicate my work to my Parents.

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ABSTRACT

Agricultural mulch films, typically made of polyethylene—derived from fossil fuels—improve crop productivity by controlling weeds and providing a microclimate. Extreme fragmentation of films imposes retrieval and disposal costs, and causes environmental problems during and after their service life. Although mulch films made of biodegradable polymers such as cellulose, (fossil fuel-based) poly (butylene adipate-co-terephthalate) and polybutylene succinate are employed in the field, the fate of biodegradation of "synthetic" additives and their impact on mechanical strength are concerns. Mulches, made of biobased polymers such as poly (lactic acid) (PLA) and PLA/ polyhydroxyalkanoate (PHA) blends, has been developed using nonwoven textile technology to address the poor mechanical properties and/or biodegradability of traditional mulch films. This dissertation focuses upon biodegradation of nonwoven mulches—spunbond (SB) and meltblown (MB)—buried in soil for 30 weeks and after exposure to simulated weathering. Soil moisture, temperature, amendments, the nonwoven processing type, color, and composition (fraction of PLA and PHA) of the mulches were evaluated in soil burial studies. The biodegradation of nonwoven mulches was characterized by the loss of tensile strength, depolymerization via hydrolysis of ester bonds and decrease of glass transition temperature, melting temperature and enthalpy of fusion. At high moisture conditions, SB mulches were recalcitrant to all the soil environmental conditions and amendments, evidenced by marginal depolymerization and insignificant loss of tensile strength. MB mulches, particularly when prepared from PLA/PHA blends, underwent the greatest (~90%) loss of tensile strength among other physico-chemical losses. Although weathered SB mulches did not undergo physico-chemical changes during simulated weathering, the rate and extent of biodegradation test under composting conditions, measured using ASTM D5338, met the compostability standard (ASTM D6400) criteria (≥ 60% biodegradation after 90 days). MB mulches experienced the greatest extent of biodegradation (> 90% after 90 days via ASTM D5338) and therefore are recommended as a "Class II" material in ASTM WK 29802, the standard specification being developed for biodegradability of agricultural plastics in soil.

TABLE OF CONTENTS

CHAPTER 1

CHAPTER 2

CHAPTER 4

CHAPTER 5

CHAPTER 6

CHAPTER 7

LIST OF TABLES

LIST OF FIGURES

CHAPTER 1

INTRODUCTION AND OBJECTIVES

1.1 AGRICULTURAL PLASTIC MULCHES

Plastic materials have many applications in agriculture, including mulch films, greenhouse construction materials, and packaging materials [1]. Plastic mulch films have been used in the agriculture since 1950s and are widely regarded as an effective method to control agrichemicals for growing crops [2]. The benefits of using plastic mulch films are: (i) soil moisture retention; (ii) increase of soil temperature; and (iii) as a weed barrier without using chemicals. The efficiency of drip or trickle irrigation has increased 50-70% [3] if plastic mulch films are employed. Some reports claim an increase in crop productivity as mulches interrupt the life cycle of insect pests, accelerate crop maturation, and channel CO_2 around the plants [4]. Plastic mulches, with a typical thickness and width of 1.25 mil (0.031mm) and 48 inches (122cm) respectively, are often prepared on rolls of 2400 feet (731 m). The width of film vary from 36 to 60 inches (91 to 152 cm) [5]. Plastic mulch films are often made from fossil fuel-based products such as low-density polyethylene (LDPE), high-density polyethylene (HDPE) and polyvinyl chloride. Over 100,000 metric tons (221 million pounds) of HDPE mulches were sold worldwide in 1992 [4]. Mulching films consumption is 130,000 tons per year in Europe and 260,000 tons per year worldwide in 2004-2005 [6]. The consumption of direct-cover and low tunnel films were around 72,000 and 75,000 tons per year, respectively [6]. A survey on Southeastern States of North America reported that 150,000 acres of land were covered with HDPE black mulches in 2000 [6]. The worldwide application of mulch films is 700,000 tons per year. To date, nearly 80% of mulched surface is found in China and the report claims 25% of growth rate of using mulches per year [7]. Mulching films can be colorless or pigmented; black films absorb more sunlight thereby reducing weeds without the need for agrichemicals, whereas white films reflect most of sunlight thereby reducing the soil surface temperature by $2^{o}C$. White mulch films are preferred over black for good productivity in summer [2]. Mechanical installation of films involves the following procedure: raising the soil bed before the seeding the plants, followed by pulling the mulch roll on top of soil-bed using tractor and finally burying the film edges. A tractor can be driven on the mulch-laid-bed to make holes for inserting plants or seeds [4].The service life of plastic mulch films is 2-3 months.

1.2 BIODEGRADABLE MULCHES (BDMs)

One of the problems in using non-biodegradable plastic mulches is the laborious retrieval of fragmented mulches after growing season. Embrittlement of mulch films leads to debris remaining in the soil indefinitely. The debris should be removed from the fields, lest they accumulate, bind to the roots, and later affect the productivity and quality of crops [4]. Environmental regulatory agencies, particularly the EPA, restrict landfills from burying PE mulches. Incineration of PE mulches is an infraction of law, albeit it is a common practice. To address these issues, mulches made of biodegradable polymers are desirable. Biodegradable mulches (BDMs) provide a great promise since they can potentially be fully mineralized by microorganisms in the soil ecosystems. *In situ* degradation of BDMs helps vegetable growers by reducing production costs. The environmental-friendly end-of-life scenario for BDMs replace poorly sustainable disposal alternatives for conventional mulches such as landfilling—and incineration, and eliminate labor costs incurred by the retrieval and disposal of plastic mulch films [2]. The factors affecting the biodegradation rate of BDMs are: (i) environmental conditions including moisture, pH, temperature, and aerobic or anaerobic conditions of the soil and; (ii) the mulch material's inherent physico-chemical properties such as chain flexibility, crystallinity, molecular weight and copolymer composition, thickness, size, and shape [8]. All of these attributes control the mechanical properties of the resulting material.

1.2.1 CURRENT BDMs IN THE MARKET

Most of the biodegradable mulch films are produced from aliphatic polyesters such as poly (butylene succinate) or (PBS) and poly (butylene succinate-co-adipate) or (PBAT).The degradation mechanism is explained in Section 2.6. In addition to biodegradability, the two reasons for employing polymer blends as feedstock to prepare mulch films are: (i) enhanced strength and/or (ii) degradability at the end of their service life [9]. Problems encountered in using biodegradable mulches include either premature breakdown of films before harvesting or long-term retention of debris after harvesting due to a slow rate of biodegradation. A few commercially available BDMs are briefly described in the following sections.

1.2.2 CELLULOSE- BASED MULCHES

Cellulose has good strength when kept dry and is low in cost; however, high hydrophilicity affects intact structure—swelling of cellulose fibers occur due to adsorption of water—leading to loss of mechanical strength. According to Shogren *et al* [10], lamination of biodegradable polymers with hydrophobic or water-resistant polymers could be a possible solution. A currently available cellulosic mulch is WeedGuardPlus® (Fig.1), produced by Sunshine Paper Company, LLC, Denver, Colorado. The fast disappearance of this mulch, well in advance of harvest, makes it poorly robust for employment in the fields [11, 12].

Figure 1: WeedGuardPlus®, a cellulosic mulch, in the open field showing premature degradation

1.2.3 STARCH-BASED MULCHES

Starch is a cheap and abundant biopolymer derived from corn and other crops. Several starch products are developed based on market demands because starch undergoes biodegradation in many environments. Atmospheric CO_2 fixed by starch-producing plants during their growth is thus recycled by their degradation or incineration, thereby completing biological carbon cycle. Gelatinized starch combined with soluble polymers such as polyvinyl alcoho4l and poly (alkylene glycols)—manufactured by Novamont in Italy under the trade name of Mater-Bi™—serve as feedstock for so-called “biodegradable” polymer [13]. Mulches made of Mater-Bi™, such as BioAgri and BioTelo (Fig.2), have been approved for use in European and Canadian organic agriculture [14].

Figure 2: Mater-Bi™ (BioTelo) in High Tunnel

1.2.4 POLY (BUTYLENE ADIPATE-CO-TEREPHTHALATE) or PBAT-BASED MULCHES

Poly (butylene adipate-co-terephthalate) or PBAT (Fig.3), an aliphatic aromatic copolyester produced by Baden Aniline and Soda Factory (BASF) from fossil fuel-based feedstock, is biodegradable under industrial composting environments (55-58^{o}C) and does not produce any residual adverse ecotoxicological effects[15]. This polymer finds agricultural applications as sheets, fibers, modifier of plastics[16], transparent films for wrapping foods, greenhouse films, plastic bags and mulch films [17]. PBAT is a major component of biodegradable plastic mulches under the trade name of Ecoflex®.

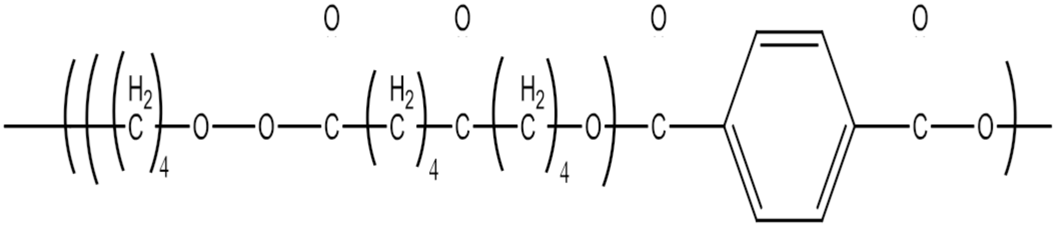


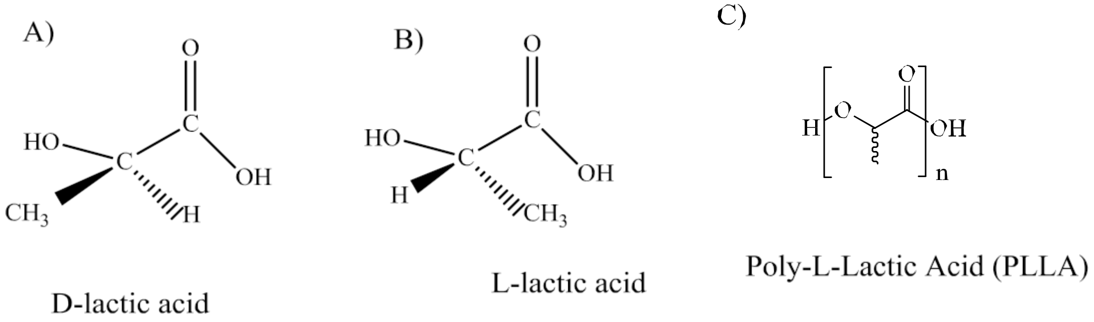
Figure 3: Molecular structure of polybutylene adipate-co-terephthalate

In 2006, a preliminary field test conducted at Michigan State University revealed Ecoflex® films were cross-linked due to the solar radiation exposure causing brittleness and subsequently premature breakdown. In addition, upon UV exposure, PBAT films were insoluble in tetrahydrofuran (THF)—the organic solvent employed as mobile phase in gel permeation chromatography to determine molecular weights (M_n)—and underwent less biodegradation tested by ASTM D5338 (Section 2.7.2.2). Due to premature breakdown (i.e., the formation of rips and tears), plots covered by Ecoflex® underwent soil moisture and heat loss, and the formation and growth of weeds [18].

1.3 POLYLACTIC ACID, POLYHYDROXYALKANOATE, AND THEIR BLENDS AS POTENTIALLY VALUABLE FEEDSTOCK FOR BDMs

1.3.1 POLYLACTIC ACID (PLA)

Fig.4 provides the structure of D and L- lactic acid (monomers of polylactic acid), in addition to poly (L-lactic acid). In L-lactic acid, the rotation of plane polarized light is in clockwise direction whereas D-lactic acid, it is in an anti-clockwise direction. D and L forms are optically *active* while DL form is optically *inactive* [19, 20]. Currently, racemic mixture of lactic acid is produced in large scale by Musashino in Japan [20]. The lactide monomer of PLA may possess either identical stereocenters i.e., L: L or D: D or enantiomeric stereocenters (L: D). PDLLA copolymer is produced by varying the composition of monomers (L and D). The presence of higher D content in copolymer (>20%) leads to completely amorphous morphology, while high crystallinity of copolymer is attributed to lower D content (< 2%) [21].



D-lactic acid

L-lactic acid

Poly-L-Lactic Acid (PLLA)

Figure 4: Molecular structure of A) D-lactic acid; B) L- lactic acid and; C) PLLA

Polylactic acid (PLA), a compostable aliphatic polyester (Fig. 4) synthesized by ring-opening polymerization (ROP), has many applications in the pharmaceutical, agricultural, and biomedical fields, mainly due to the effort of DuPont and Ethicon [22]. Lactic acid, the monomer of PLA, is predominantly available from renewable sources such as sugar beet, cane sugar, starch, and cellulose and fermentation of glucose contained in the above-mentioned agricultural products. Thus, PLA, in terms of sustainability and a cradle-to-grave perspective, emits net zero CO_2, thereby reducing the production of greenhouse gas [19, 23].

NatureWorks, LLC—located in Blair, Nebraska, USA with the production capacity of 140 000 tons/year—manufacture 15 plant- based Ingeo™ PLA biopolymers. The inclusion of “PLA” in the Ingeo™ product name designates the biopolymer contains polylactic acid. Ingeo™ grades are deemed “certified compostable PLA polymers” by Biodegradable Plastics Institute (BPI), by fulfilling the requirements of ASTM D6400 specifications. Because of its high environmental sustainability, abundance, relatively low-cost compared to other polymers, and compostability, PLA is considered as a viable biopolymer to prepare BDMs. PLA has many non-ideal properties. PLA is fully biodegradable only under composting conditions i.e., at a temperature $> 59^oC$ [24]. In addition, it possesses inferior physical properties such as low thermal stability, high rigidity, high brittleness, high glass transition temperature (T_g), and low melting temperature (T_m). However, a positive report on the biodegradation of PLA at ambient temperature has been given for a mixed compost culture [25].

1.3.2 POLYHYDROXYALKANOATE (PHA)

Polyhydroxyalkanoate (PHA) (Fig.5) is an energy storage product of algae and bacteria. PHA is a generic term for the biopolymers such as polyhydroxybutyrate (PHB) and polyhydroxyvalerate (PHV). After discovery in 1926 by French bacteriologist and chemist Maurice Lemoigne, the British Imperial company Imperial Chemical Industries (ICI) developed a bioplastic called biopol from PHB in 1990. It underwent biodegradation in the soil at the highest rate. PHA received interest from corporations such as DuPont, Proctor and Gamble, and Exxon for the large-scale commercial production. However, the viable and economical production of PHB has yet to be developed due to higher price and/or lower performance compared to petroleum-based plastics.

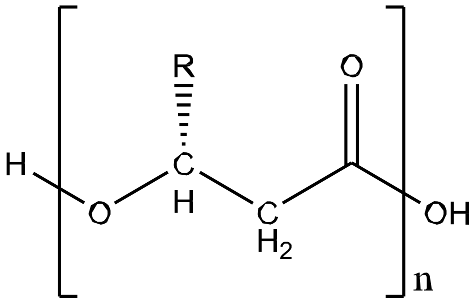


Figure 5: Molecular Structure of polyhydroxyalkanoate (PHA) (R=alkyl group)

Mirel™ is a bioplastic made from PHA by Metabolix in Cambridge, MA, USA. PHA possesses undesirable mechanical properties to use as a biodegradable mulch feedstock such as high crystallinity causing brittleness, low melt viscosity, and thermal instability [26].

In this dissertation, authors have used PHA feedstock obtained from Tianjin Greenbio Material Co (Tianjin, China). PHA feedstock, commercially known as GreenBio, consists of a copolymer of 3-hydroxy butyrate and 4-hydroxy butyrate (Fig.6); the latter monomeric unit being present at < 30%, possessing a number-averaged molecular weight (M_n) of 446,000, which is believed to decrease rapidly upon melt extrusion [27, 28].

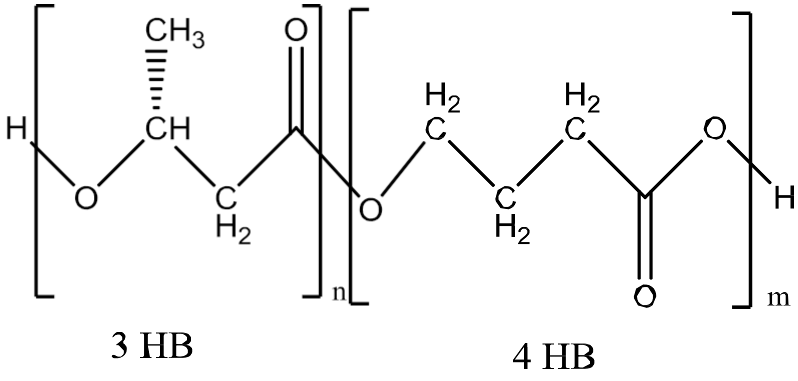


Figure 6: Molecular structure of poly (3-hydroxybutyrate-*co*-4-hydroxybutyrate) P(3HB-*co*-4HB) [The indices *n* and *m* refer to the number of repeat units for 3-hydroxybutyrate and 4-hydroxybutyrate, respectively]

1.3.3 PLA/PHA BLENDS AS BDMs

The difficulty in controlling the hydrolysis rate, poor hydrophilicity, and high rigidity of PLA and high embrittlement of PHA restricted the usage of the two polymers as hompolymeric feedstocks for mulches. Most viable ways to improve the performance of PLA are: (i) incorporate covalent modifications such as grafting reactions and copolymerization and (ii) blending with other polymers and plasticizers. The blendsing of PLA and PHA reduces the deficiencies of each polymer when used individually, and is therefore of great potential commercial interest. For example, the shortcomings of PLA such as hardness and brittleness can be overcome by blending with the more ductile PHA [29]. In general, addition of PHA to PLA enhances biodegradability, while the addition of PLA provides strength and reduces tack for PHA during processing [30, 31]. Tackiness is the property of a polymer, compound, or adhesive causing two layers to stick together on application of mild pressure. Tacky polymers or compounds do not necessarily stick to other surfaces [32]. However, there are limitations to the proportions for blending polymers. The PHA content in the blends increases the crystallinity, thereby decreasing in elongation at breakage. There are reports where optimum PHA content of 10% maintains the toughness of blends without compromising the strength [33, 34].

1.4 OBJECTIVES

In this dissertation, experimental BDMs formed from PLA/PHA blends have been prepared and tested for biodegradation in the soil burial study under greenhouse conditions. The goal of this project is to study the performance of agricultural mulches prepared from PLA and PLA/ PHA blends as potentially valuable BDMs. In this project, nonwoven prepared using nonwoven textile technology leading to enhanced strength and low mass per unit area are used. The overall goal encompasses the following specific objectives.

1. To understand the process for biodegradation for meltblown and spunbond nonwoven agricultural mulches, made of biodegradable polymers polylactic acid (PLA) and PLA/polyhydroxyalkanoate (PHA) blends at different proportions, in soil burial studies under greenhouse conditions.
2. To determine the importance of several important variables on the process of biodegradation including soil temperature, soil moisture, ultraviolet radiation, and application of pineapple juice (as an enzyme source and carbon energy source).
3. To understand the effect of biopolymer type, composition and nonwoven processing approach, on biodegradability.
4. To understand the biodegradation of nonwoven mulches under composting conditions after exposed to simulated weathering.

1.5 ORGANIZATION OF THIS DISSERTATION

This dissertation is divided into the following chapters.

Chapter 1:	Introduction and Objectives
Chapter 2:	Literature review including hypothesis and preliminary soil burial study.
Chapter 3:	Soil burial study evaluating the effect of soil moisture and amendments on the biodegradation of PLA and PLA/PHA blends based nonwoven mulches
Chapter 4:	Comparison of biodegradability of PLA and PLA/PHA based nonwoven mulches to a commercially available starch-based BioTelo mulch.
Chapter 5:	Comparison of biodegradation to abiotic hydrolysis of nonwoven mulch.
Chapter 6:	Effect of soil temperature on biodegradation of PLA meltblown nonwoven mulches.
Chapter 7:	Kinetics of biodegradation for nonwoven mulches.

Chapter 8: Effect of simulated weathering on physico-chemical properties and inherent biodegradation of PLA and PLA/PHA nonwoven mulches.

Chapter 9: Conclusions and Recommendations.

CHAPTER 2

LITERATURE REVIEW

2.1 INTRODUCTION

This chapter encompasses processing of PLA, preparing blends of PLA with other polymers and plasticizers and brief details of the mechanical properties for PLA and its blends. The production and processing variables for two types of nonwoven, meltblown (MB) and spunbond (SB), and their differences are discussed. Biodegradation, standards for biodegradable plastics, testing methods used to evaluate the biodegradable material, compostable plastics, and composting conditions are discussed in detail in the last part of this chapter.

2.2 PROCESSING OF PLA

A complete review of the processing of PLA is given elsewhere [35-38] and is beyond the scope of this review. The most important techniques used for processing of PLA are:

1. Drying and extrusion;
2. Injection-molding;
3. Blow-molding;
4. Fiber-spinning and production of nonwoven;

For the above-mentioned processing techniques, the starting material should possess high thermal stability to prevent degradation and maintain molecular weight and properties. Neat PLA undergoes thermal degradation above 200^{o}C, which results in low molecular weight because of chain scission. PLA possesses inferior properties such as high crystallinity leading to brittleness, very low impact resistance, thermal stability, and flexibility. The difficulty in enhancing the low hydrolysis rate, poor hydrophilicity and high rigidity restricted applications of PLA. Therefore, PLA blended with other polymers or plasticized PLA is preferred for a wide range of applications [39-41].

2.3 BLENDING AND PLASTICIZATION

PLA (frequently enriched in L-lactic acid monomeric units) is commonly modified by blending with other polymers or adding plasticizer. *Blending* is defined as creating a "macroscopically homogenous mixture of two or more different species of polymer"[42] and *plasticizer* as "substance or material incorporated in a material to increase its flexibility and workability. Plasticizer may reduce the melt viscosity and lower elastic modulus of the product"[43].The processing temperature for PLA homopolymers, for example, in blow or injection molding, thermoforming, and extrusion is 185-190^{o}C. (L- and D-PLA homopolymers possess glass transition temperature and melting temperature of 55^{o}C and 175^{o}C, respectively). The high processing temperatures lead to depolymerization, hence poor thermostability. In addition to blending and addition of plasticizer, the narrow processing window of PLA can be rectified by inducing melting point depression by incorporating a small amount of D-lactide to L-lactide, or vice versa, in the polymerization feedstock, leading to PDLLA copolymer [44]. The strong interaction between enantiomeric PLAs i.e., PDLA and PLLA form a stereo complex copolymers with melting temperature of 220-230^{o}C. PDLA/PLLA blends possess higher hydrolysis resistance and thermostability than pure PLLA or PDLA [45].

Another common strategy to modify PLA properties is by copolymerization of PLA with another polymer. Although covalent modification, particularly copolymerization, can offer better performing polymers than those produced by blending, it necessitates the knowledge to control the polymerization reaction. Thus, polymer blending is viewed as a less expensive alternate strategy [46, 47]. To overcome these deficiencies, PLA has been blended with several different biodegradable polymers such as starch, chitosan, polyethylene glycol (PEG) or polyethylene oxide (PEO)[48] and poly (ε-caprolactone) (PCL) [46]. Polymers such as PHB [49, 50], polyvinyl acetate (PVA), polymethyl methacrylate, polyamide [40] form a complete miscible blends with poly(L-lactic acid) (PLLA) [51]. Blending of PLA with non-biodegradable polymers such as organophilic montmorillonite clay [39] and poly(p-vinyl phenol) [41] were also investigated. An overview of PLA blended and/or plasticized with other polymers is briefly discussed below in Table 1.

Table 1: PLA blended with other polymers and plasticizers with brief descriptions of physical properties of blends

BLENDING AGENT	BLEND'S PHYSICAL PROPERTIES
Starch	Starch can be good particulate filler in polymer blending system due to small granular size. PLA can be blended with 45% starch only in the presence of compatabilizing agent such as oligomeric acid (OLA), glycerol and methylenediphenyl diisocyanate (MDI). The resulting polymer blends possesses morphology of smooth structure and high tensile strength and elongation at breakage (EB). However, the high moisture content of starch (10-20%) affects the compatibilizing agent (MDI) and the mechanical properties of PLA[52].
Chitosan	Although PLA/chitosan blends are readily absorbed by tissues, it exhibits poor soft tissue compatibility due to its high crystallinity and the low hydrophilicity of PLA. In addition, this blends show a reduced degradation rate. The melt blending process for the production of PLA/chitosan blends results in the poor mechanical properties such as low tensile strength and EB; however, a high tensile modulus without substantial miscibility is obtained [53].
poly(ε-caprolactone)	Blending of PLA and PCL at different weight percentages such as 100/0, 80/20, 60/40, and 50/50 increased EB; however, other mechanical properties such as elastic modulus and break strength decreased. The slower degradation rate of PCL than PLA has limited the blends application only to implants for the long-term employment [54].

Table 1 Continued: PLA blended with other polymers and plasticizers with brief descriptions of physical properties of blends

BLENDING AGENT	BLEND'S PHYSICAL PROPERTIES
Poly(butylene adipate-co-terephtalate) or PBAT	The brittleness of PLA is improved by blendsing with PBAT. However, there is substantial reduction in tensile strength in contrast to EB. PBAT, weight percentage of less than or equal to 2.5, form a complete miscible blends with PLA. The degree of crystallinity of PLA decreased when the PBAT content was increased [55].
Epoxidized soy bean oil (ESO)	ESO decreased the glass transition temperature (T_g) of PLA.EB of PLA has increased on blending ESO with PLA. The dominant plasticization effect of ESO is reflected from the reduction of storage modulus and viscosity of blends [56].
Polyethylene glycol or PEG	Branched (by adding peroxides in extrusion process) and linear PLA was plasticized with various concentrations of PEG (5, 10, and 15 wt %). The storage modulus was decreased on increasing the PEG; thus, the viscosity and elastic properties of plasticized PLA were decreased. In general, plasticizers decrease the T_g of polymers; thus, PEG decreased T_g of linear and branched PLA [57].

Table 1 Continued: PLA blended with other polymers and plasticizers with brief descriptions of physical properties of blends

BLENDING AGENT	BLEND'S PHYSICAL PROPERTIES
Citrate esters	Citrate esters, in general, are considered as low molecular weight plasticizers. Citrate esters such as triethyl citrate, tributyl citrate, acetyl triethyl citrate, and acetyl tributyl citrate by weight percentage of 10, 20 and 30 were plasticized with PLA. Triethyl citrate of 30% had a profound effect of reducing the T_g by 28.9%, T_m by12%, tensile strength by 86% and increasing EB by 86% [58].

2.4 NONWOVEN TECHNOLOGY

In general, nonwoven are defined as a sheet or web structure made by bonding and interlocking fibers by mechanical, thermal, chemical- or solvent-means. The European Disposables And Nonwoven Association (EDANA), akin to the International Organization for Standardization (ISO) , defines a nonwoven material as " a manufactured sheet, web or batt of directionally or randomly orientated fibers (not yarns or rovings) bonded by friction and/or cohesion and/or adhesion" [59]. Nonwoven processing mainly involve two stages: (i) web formation; and (ii) consolidation. A web can be formed from randomly or directionally oriented fibers by the following three processing methods: (i) *dry-laid processing* -originated from textiles industry; (ii) *wet-laid processing*- originated from papermaking industry; and (iii) *polymer-laid processing* - originated from polymer extrusion and plastics [60, 61]; and it consists of following spun-melt technologies:

1. Spunbonding;
2. Meltblowing;

3. Electrospinning;

After a web is formed, it can be consolidated using one or more of the following means: chemical, solvent, thermal and mechanical bonding. The fibers most commonly used for this technology are cellulose, cotton and many synthetic fibers including polyurethane, polyethylene, polyester, and nylon or mixtures thereof [62]. Mats, fabrics composed of thermoplastic and finished products are often nonwoven. The robust production of nonwoven is due to the coordination between fiber producers, nonwoven producers, binder producers, and machinery manufacturers [63]. One of the most difficult tasks in nonwoven manufacturing is production of textiles with small fiber diameter. The surface area of a fiber scales linearly with diameter, the volume scales with square of the diameter, and the specific surface area(s) varies inversely with diameter (d); thus, the higher specific area nonwoven possess finer fibers and subsequently high surface functionalization (e.g. altering the surface characteristics by treating with gas plasma and zinc oxide sputter coating). The measurement and control of fiber diameters are of great interest because of the impact of the properties of finished webs. In addition, the fiber strength, porosity, average fiber length, and fiber entanglement density play equal role in determining the applications of fiber in filtration, membrane separation, protective clothing, wound dressings and precession wipes [64, 65]. Electrospinning, meltblowing, and spunbonding are most commercially used processes to prepare nonwoven by polymer laid.

Electrospinning involves applying a strong electric potential of more than 10kV to a polymer solution contained in a syringe to force a jet of solution onto a grounded screen located few centimeters away. Rapid evaporation of the solvent results in nonwoven of ultra-fine fibers diameter of nanometer range.

In *meltblowing*, fibers are produced in a single step by extruding polymer melt through an orifice die and drawing down the extrudate with the jet of hot air with the temperature, same as polymer melt (Section 2.4.1.2). The fiber diameter is usually 1-7 µm.

Spunbonding involves three generic process (i) melt spinning-fibers of thermoplastic polymers is extruded in a cold air to cool and solidify the filaments; (ii) dry spinning-continuous extrusion of fiber forming polymer in the heated chamber to remove solvents that forms solid filament and; (iii) wet spinning-continuous extrusion of fiber forming polymer in the liquid coagulating medium that generates the polymer. The fiber diameter is usually in the range of 1-50 µm; but, 15-35 µm is desired [65]. The spunbonding and meltblowing processes are explained in detail below.

2.4.1 SPUNBONDING (SB) PROCESS

The spunbond process was developed simultaneously in both Europe and USA in the 1950's. However, its importance was recognized and commercialized only in the mid-60s and early70s, evident from the increased number of patents filed. Four major operations must be controlled simultaneously in the production of spunbond webs: (i) filament extrusion; (ii) drawing; (iii) laying down; and (iv) bonding. The first three operations are a typical synthetic fiber spinning operation that constitutes the major web formation phase. The latter operation is web consolidation or bond phase of the process that produces material; thus, the common name "spunbond" has been used for the process [63, 66].

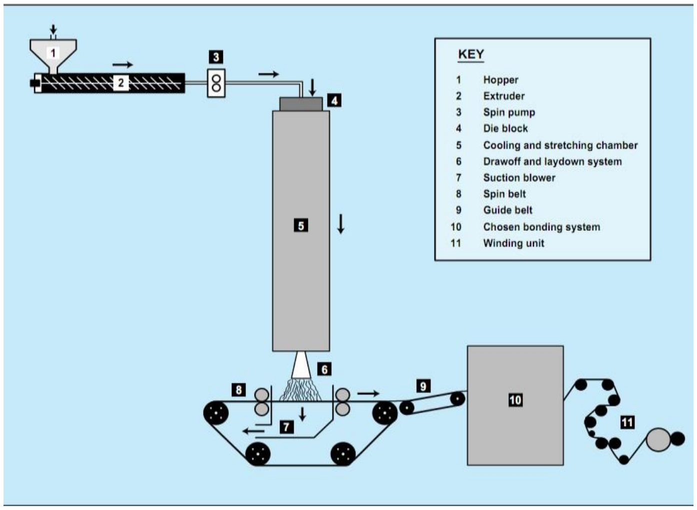


Figure 7: Schematic of a typical spunbond process [63]

The basic spunbond processing line consists of following components: a filament forming extruder; a metering pump; a die assembly; a filament spinning unit; drawing and deposition system; a belt for collecting filaments; a bonding zone; and a winding unit (Fig.7).

The die block assembly, one of the most important elements in the spunbond process, receives polymer melt from the extruder and metering pump. The die block assembly consists of two distinct components: polymer feed distribution system and the spinneret block. The feed distribution system delivers a uniform polymer melt to the spinneret block. The critical steps such as filament spinning, drawing, and deposition are integrated into a single system to solidify, draw, and entangle the extruded filaments from the spinneret and deposit them into conveyor belt (Fig.7). The details of the each operation are described elsewhere [63].

2.4.2 MELTBLOWING (MB) PROCESS

In the early 50s, meltblowing nonwoven technology was developed to prepare microfiber filters for collecting radioactive particles formed on the upper atmosphere. These fibrous materials are generally less than 10μm in diameter and found in nature in the form of spiders silk and pineapple leaves [67]. Esso research and Engineering Company (now Exxon-Mobil Co.) in the late 1960s acknowledged the potential value of these microfibrous materials and developed the least expensive method generating blown microfibers from polypropylene. Exxon patented the technology after extensive research carried out by Wente *et al* [68] based on microfiber technology.

The schematic MB process developed by Exxon is shown in Fig.8. The processing equipment consists of the following components: an extruder; a metering pump; a die assembly; and web formation and winding equipment. A uniform polymer melt is delivered to the die assembly by an extruder and metering pump. The die assembly has three components: (i) a feed distribution system; (ii) a die nosepiece and (iii) air manifolds. The melt polymer is uniformly distributed to the die nose by polymer feed distribution system. High velocity hot air, generated by air compressor, is supplied by air manifolds entering on top and bottom side of the die nosepiece. When the molten polymer is extruded from the die holes, high velocity hot air attenuates this polymer stream to form microfibers. When the hot air with its microfibers approaches the collector screen, it absorbs a large amount of surrounding air that cools and solidifies the fibers that consequently laid the random fibers (self-bonded nonwoven web) on the collecting screen. Fibers in the MB web are intact due to the combination of entanglement and cohesive bonding. The high randomness and entanglement are due to the high turbulence of air biased in the machine direction by the moving collector. A variety of MB webs is produced by changing the collector's speed and collector's distance from die nosepiece. To draw the hot air and enhance the fiber laying process, a vacuum is applied inside the collecting screen. The MB web is wound on the cardboard tube and processed based on the end-use -requirement. The fiber entanglement and fiber-to-fiber bonding produce a web that requires no further bonding. However, the web can be thermally calendered with a smooth or patterned finish or can be thermally laminated with other substrates.

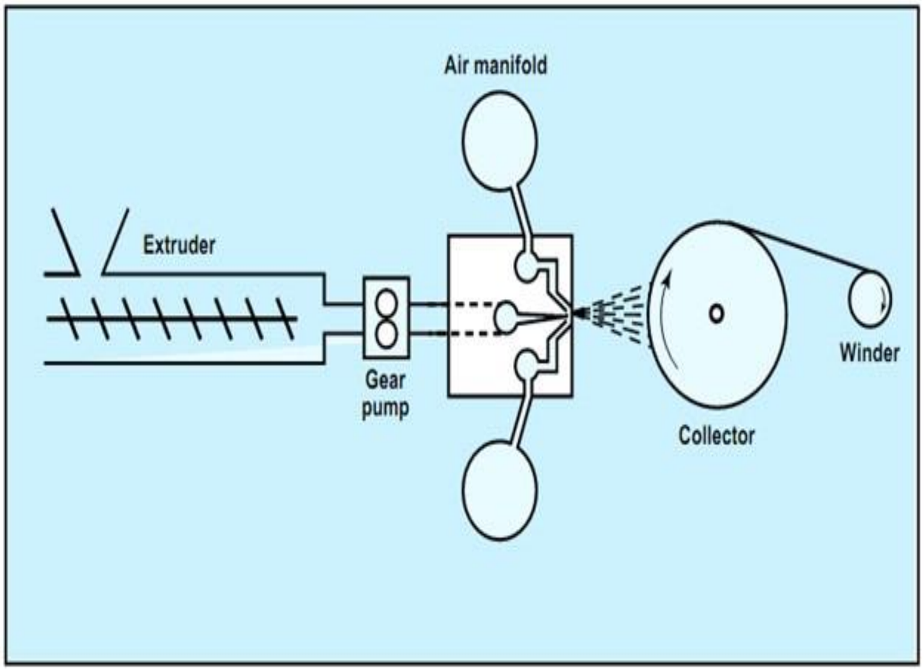


Figure 8: Schematic of Exxon's meltblowing process [63]

2.4.3 VARIABLES IN SPUNBOND AND MELTBLOWN, AND CHARACTERISTICS OF THE PROCESS

The complex spunbond and meltblown processes are controlled by many operating variables. The processing variables in both processes are divided into two categories: (i) operational variables; and (ii) material variables. A variety of SB and MB products with the desirable qualities can be produced by manipulating these variables. The process economics and product reliability necessitate the optimization and precise definition of these variables. The major process variables affecting filaments and web properties of SB and MB process are: (i) polymer characteristics; (ii) melt viscosity and temperature; (iii) air temperature and flow rate; (iv) filament draw speed; (v) polymer throughput rate, and collection speed.

2.4.3.1 CHARACTERISTICS AND PROPERTIES OF SPUNBOND AND MELTBLOWN WEBS

Although SB and MB nonwoven share common end-user applications in medical fabrics and sanitary products, there are indigenous differences in the characteristics and properties webs or staple fibers. Table 2 list major differences between SB and MB processes.

Table 2: Differences between spunbond and meltblown webs [63]

SPUNBOND (SB) WEBS	MELTBLOWN (MB) WEBS
Random fibrous structure.	Random fiber orientation.
Generally, white with high opacity per unit area.	Highly opaque (having a high cover factor)
Higher ratio of strength to weight	Low to moderate strength.
High tear strength.	Low tear strength.
Basis weight typically ranges from 8 to 350 (g/m^2).	Basis weight typically ranges from 5 to 200 (g/m^2).
Fiber diameter ranges from 15 to 40 microns.	Fiber diameter ranges from 2 to 10 µm.
Linear density of fiber density ranges from 0.5 to 20 decitex	Linear density of fiber density is 0.05 to 2 decitex.
Smaller volume of air close to ambient temperature is applied first to quench and then to attenuate the fibers.	Large amounts of high-temperature air are used to attenuate the filament[1]
Requires 2-3 kWh/kg electrical energy per pound of web.	Requires 7-8 kWh/ kg electrical energy due to the hot air necessity in the attenuation. This subsequently leads to high production cost.

1. The air temperature is equal or slightly greater than the melting temperature of the polymer

2.4.4 COMPARISON OF PLA-BASED NONWOVENS TO CONVENTIONAL NONWOVENS

PLA nonwoven possesses superior mechanical properties compared to poly (ethylene terephthalate) (PET).

Hydrophilicity
Drapeability
Resilience
Processability
Controllable shrinkage
Tenacity up to 7 g/den
Excellent crimp retention (i.e., the waviness of fiber where the axis of a fiber under minimum external stress departs from a straight line and follows a simple or a complex or an irregular wavy path). A higher number of crimps per inch indicate a finer fiber [69]
Dyeable with dispersion dyes
Low flammability and smoke generation
Thermal bonding temperature can be controlled
Elastic recovery
Low density compared to PET [70]
Very low resistance to abrasion

The last property of PLA fibers—low resistance to abrasion—is useful in the carpet industry for attracting the environmentally conscious buyers [71]. Generally, “BD nonwoven” fabrics find applications in industrial wipes, filters, floor coverings, thermal insulations, protective clothing, geotextiles, medical applications such as surgical gowns, drapes, face masks, and reinforcements in structural composites, personal hygiene products such as disposable diapers, erosion control and in landscaping [59, 72].

2.5 BIODEGRADABILITY OF PLASTICS IN SOIL

2.5.1 INTRODUCTION

There have been significant developments in the production of synthetic polymers since 1940s. Plasticulture is defined as "a system of growing crops wherein a significant benefit is derived from products of plastic polymers" [73]. Nearly 2-3 million tons of plastics have been used in agricultural applications such as coverings for greenhouse or high tunnels over crop rows, silage covers, drip-irrigation tubing, drip tape, hay bales, nursery pots, packaging materials, container for growing transplants and in mulching [18]. In 2004, the consumption of plastics in agriculture had reached 615,000 tonnes per year [74]. In Europe, 1,500,000 tonnes of all polymers have been used in agriculture and horticulture annually from 2009-2010 [75]. Plastic materials made of fossil fuel-based polymers such as polyethylene (PE), poly (vinyl chloride), and co-polymers of ethylene and vinyl acetate are primarily used as films in agriculture [76, 77]. Despite the advances in synthesis, manufacture, and processing of the polymers, two concerns still confront the polymer industries: (i) use of non-renewable and fossil fuel-based chemicals to manufacture polymers; and (ii) the fate of plastic wastes. The three common disposal methods for plastic wastes are incineration, recycling and landfilling [78]. Thus, waste materials formed from agricultural plastic wastes after their useful lifetime are either incineration or landfill disposal [79]. A few alternate end-of-life options are biodegradation under ambient soil conditions and composting; however, high cost, poor biodegradability of many fossil fuel-based polymers, and difficulty in the removal of debris formed from the brittle polymer films hinder these choices [80, 81]. A solution is the introduction of biobased and biodegradable polymers, to increase the sustainability of agricultural practices by reducing the accumulation of non-biobased and non-biodegradable plastic wastes. In addition, the disposal problems of conventional plastics can also be eliminated [24, 77, 82, 83]. If the end-of-life fate for the biobased plastics is in landfills or buried in the soil, the extent and rate of biodegradability of plastics and their additives such as plasticizers and colorants used in the process of synthesis should be known.

2.5.2 GENERAL MECHANISM OF PLASTIC BIODEGRADATION

The term “*biodegradable plastics*” refers water-insoluble polymer based materials (plastics) that are degraded by microorganisms. Two properties of polymers, water insolubility and large molecular size, prevent their transport through the cell wall of microorganisms. An alternative route for microbial assimilation is the secretion of extracellular enzymes leading to depolymerize the polymers and generate water-soluble intermediates for easy transport and utilization in appropriate metabolic pathways (Fig.9).

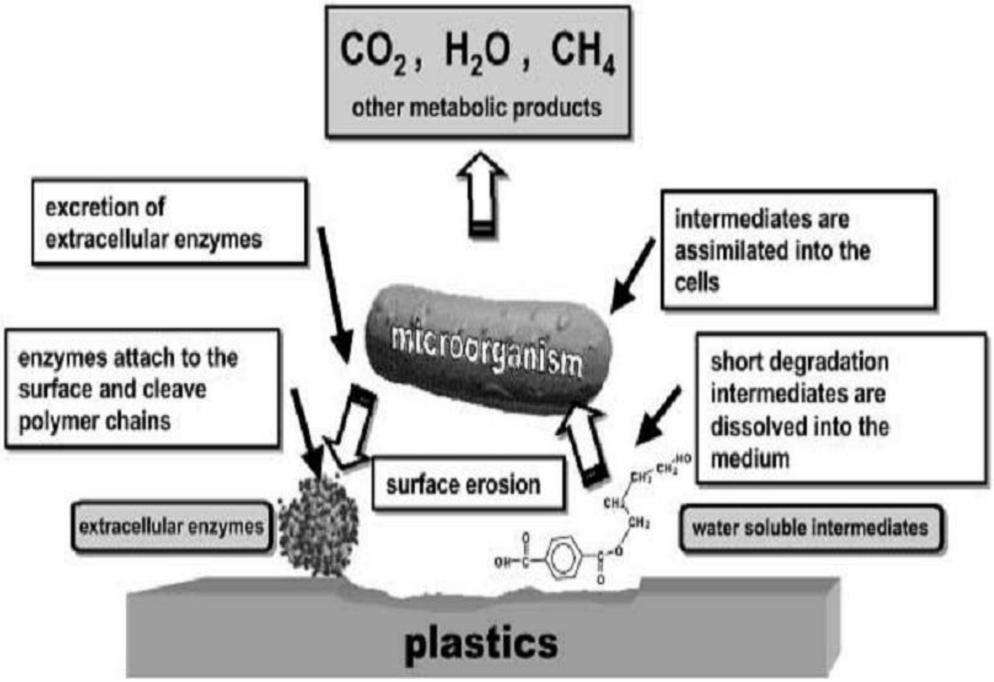


Figure 9:General mechanism of plastic biodegradation[84]

The end products of the reaction are typically CO_2, methane (through anaerobic degradation), water, and new biomass (Eqs.1and 2) [84].

$$C_{\text{polymer}} + O_2 \xrightarrow{\text{microorganisms}} CO_2 + H_2O + C_{\text{residue}} + C_{\text{biomass}} \qquad \text{Aerobic biodegradation (1)}$$

$$C_{\text{polymer}} \quad {}^{\text{microorganisms}} \quad CO_2 + H_2O + CH_4 + C_{\text{residue}} + C_{\text{biomass}} \qquad \textbf{Anaerobic biodegradation} \quad 2$$

C_{polymer}, C_{residue}, and C_{biomass} are the carbons in polymer, residue and in the biomass, respectively.

Unless the molecular weight of polymers is greatly reduced, thereby forming water-soluble intermediates, polymeric materials cannot be transported into cells [84]. Extracellular enzymes act on a polymeric material's surface due to their inability to penetrate deep inside the polymeric material, thereby defining biodegradation of plastics as a surface erosion process. Enzyme-catalyzed depolymerization is the primary process of biodegradation. In addition, abiotic chemical and physical processes such as hydrolysis, thermal polymer degradation, and oxidation or scission of polymer chains by irradiation (photodegradation) take place in either parallel or as a first stage during the process of biodegradation [85]. Environmental factors such as humidity, temperature, pH, salinity, availability of oxygen, the supply of different nutrients influence microbial degradation and need to be considered.

Another factor of the complex plastic degradation process is the supramolecular structure and composition of plastic materials. In most cases, the plastic materials are either blends of different polymers or mixtures containing low molecular weight additives (plasticizers). In addition, co-polymers such as "random" (statistical distribution of structural elements along the polymer chains), "block" (oligo-homopolymer subunits linked by covalent bonds), and "cross-linked" (branching of chains or formation of network through the inclusion of multifunctional monomer units) can be employed. Although the overall compositions of the aforementioned different co-polymers are similar, the different structural arrangement of these polymers can affect the biodegradability.

Further, parameters reflect the degree of ordered structures within polymeric materials such as crystallinity and T_g affect the biodegradability. The processing conditions also affect the degree of crystallinity. Thus, biodegradability is a highly complex process because of the influence of all the above factors and requires eclectic knowledge for testing the biodegradation of plastics and interpretation of results. The standardized evaluation of biodegradable plastics must be based on definitions, and what biodegradation means regard to the material [84].

2.5.3 HYPOTHESIS: DEGRADATION OF PLA MULCHES VIA A THREE STAGE PROCESS

The working hypothesis for the process of biodegradation of PLA-based nonwoven mulches, developed by Hayes *et al* [86], given in Fig.10, divides the process into 3 stages.

I. The first stage, partial fragmentation, is attributed to abiotic factor: sunlight and moisture. Microorganism colonies are initiated during this stage

II. After significant fragmentation in the second stage, microbial assimilation starts.

III. The final stage of this process is the mineralization converting PLA into CO_2, water and biomass.

The first stage of mechanistic model appears to be consistent with the trends observed from the soil burial studies (Chapters 3-7). The soil burial studies contained in this dissertation were conducted to understand the events occurring in stage one and how they differ between mulches.

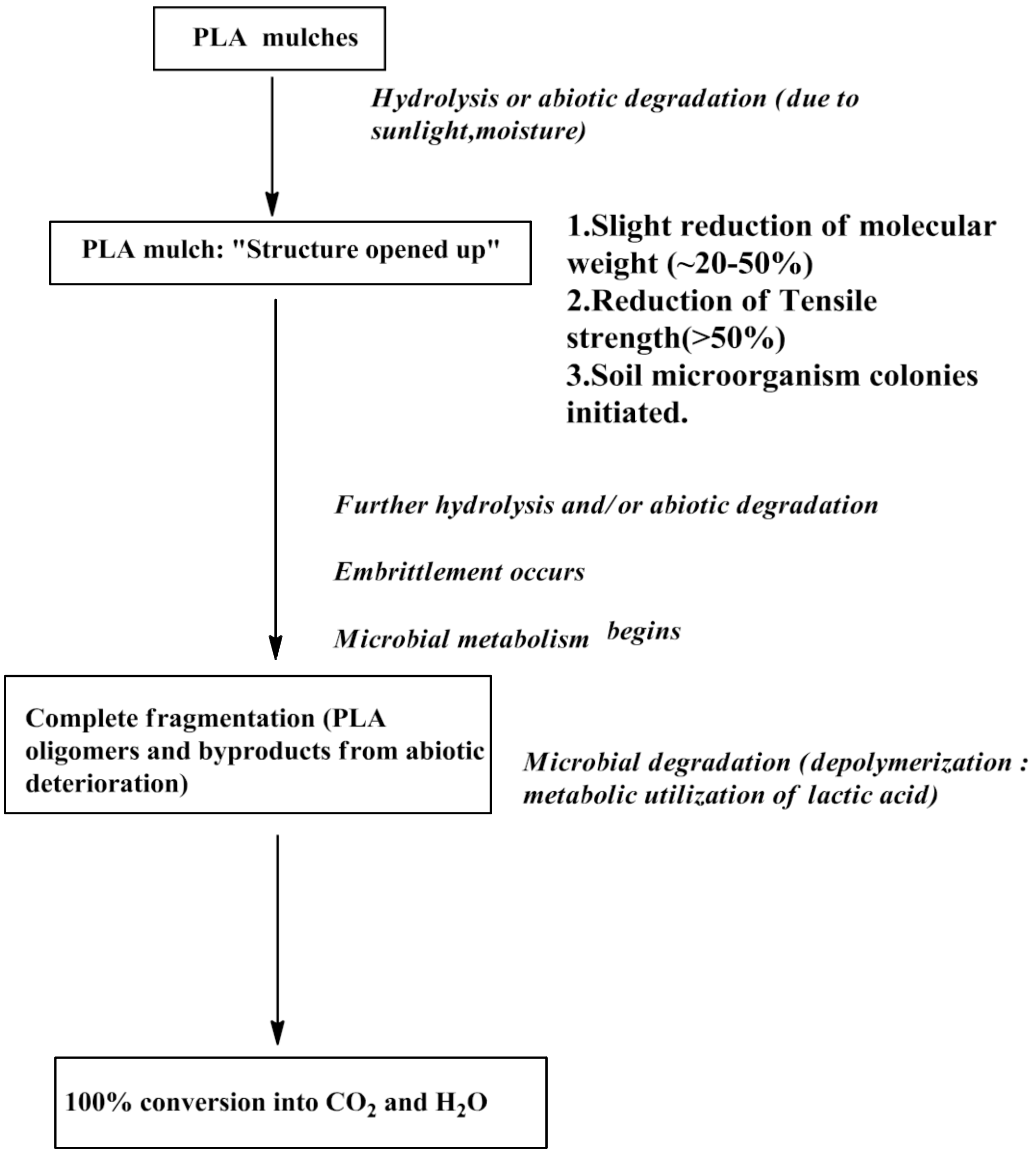


Figure 10: Mechanistic model for biodegradation of PLA mulches [86]

2.5.4 FORMAL DEFINITIONS OF BIODEGRADABILITY

In 1992, biodegradable polymer experts from around the world gathered for an international workshop to achieve a consensus on definitions, standards, and testing methodologies. After the successful meeting that included manufacturers, laboratories, environmentalists and standard organizations in Europe, USA, and Japan, there was a general agreement on few key points such as:

To apply a definition for practical purpose, a biodegradable material should be related to a specific disposal pathway such as composting, sewage treatment, denitrification or anaerobic sludge treatment.

The rate of degradation of materials, manufactured to be biodegradable, has to be consistent with the disposal method and other components of pathway to which it is introduced to control accumulation.

CO_2, water, and minerals are the final products of aerobic biodegradation and biomass and humic materials are the intermediate products.

Biodegradable materials should not leave any toxic products affecting the disposal process.

These key points encouraged the development of the standards for biodegradable plastics that add a specific period, disposal pathways, and test methods into definitions [87]. The American Society for Testing and Materials (ASTM) and other international regulatory agencies (Table 3) have prepared the standardized definitions for the terms “biodegradable plastics” and “biodegradability”. While ISO definition of biodegradable plastics requires only the chemical change in the material (e.g. oxidation) by microorganisms, the conversion of plastics to microbial metabolic products are defined in European Standardization committee (CEN) and German institute for standardization (DIN) standards for biodegradable plastics.

Table 3: Definitions used in correlation with biodegradable plastics (or polymers)

Organization	Definition
ASTM Subcommittee D20-96	**Biodegradable plastics:** A degradable plastic in which the degradation results from the action of naturally occurring microorganisms such as bacteria, fungi and algae [88].
ISO 472-1988	**Biodegradable plastics:** A plastic designed to undergo a significant change in its chemical structure under specific environmental conditions resulting in a loss of some properties that may vary as measured by standard test methods appropriate to the plastic and the application in a period of time that determines its classification. The change in the chemical structure results from the action of naturally occurring microorganisms [89].
Japanese Biodegradable plastics society	**Biodegradable plastics:** Polymeric materials are converted to low molecular weight compounds where atleast one step in the degradation process is through metabolism in the presence of naturally occurring microorganism [90].

Table 3 Continued: Definitions used in correlation with biodegradable plastics (or polymers)

Organization	Definition
European Standardization committee (CEN)	**Biodegradable plastics:** A degradable material in which the degradation results from the action of microorganisms and ultimately the material is converted to water, carbon dioxide and/or methane and a new cell biomass [84, 89]. **Biodegradation:** Biodegradation is a degradation caused by biological activity, especially by Fg nm enzymatic action, leading to a significant change in the chemical structure of a material [91]. **Inherent biodegradability:** The potential of a material to be biodegraded, established under laboratory conditions [84, 91]. **Ultimate biodegradability:** The breakdown of an organic chemical compound by microorganisms in the presence of oxygen to carbon dioxide, water and mineral salts of any other elements present (mineralization) and new biomass or in the absence of oxygen to CO_2, methane, mineral salts, and new biomass [84, 91].

2.5.5 GENERAL PRINCIPLES OF TESTING THE BIODEGRADABLE PLASTICS

The conditions employed for biodegradation tests and their results are always variable, albeit conducted to evaluate the degradation phenomena of plastics. The tests, in general, are divided into three categories: field; simulation; and laboratory test (Fig.11).

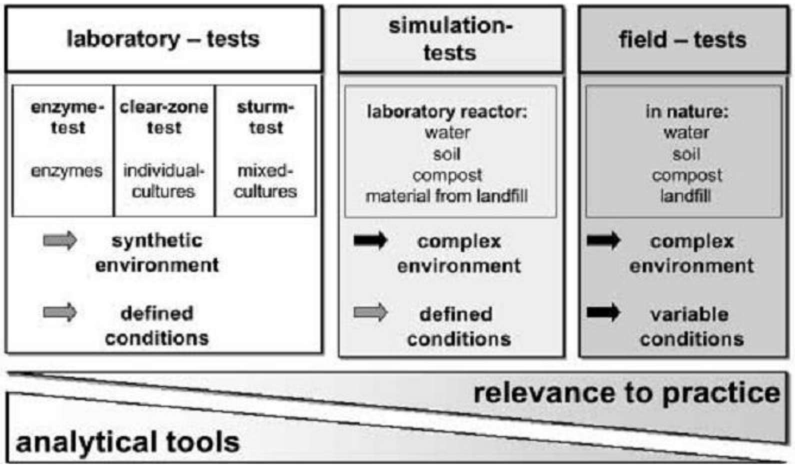


Figure 11:Schematic overview of tests for biodegradable plastics [84]

2.5.5.1 FIELD TESTS

Field tests involve burying the plastics in the soil, placing them in a river or lake, or performing a full scale composting process upon them. The disadvantages of this category of testing, relative to the other categories listed in Fig.11, are the inability to control environmental parameters such as temperature, humidity and pH, and the difficulty of finding measurable parameters for monitoring the biodegradation process. The possible methods to evaluate degradation are observing the visible changes in the polymer or measuring its weight loss to determine the disintegration. If the material undergoes fragmentation or contains strongly adsorbed soil particles, it leads to serious quantitative error in the recovery from compost, water, or soil, thereby hindering the measurement of weight loss. Physical deterioration is not necessarily equivalent to biodegradation. For instance, polyethylene films—used in the field study of TN—

underwent loss of tensile strength; however, it was not considered to be biodegradation [4]. Hence, this type of test cannot serve as a proof of biodegradability.

2.5.5.2 SIMULATION TESTS

This category of testing evaluates the degradation under laboratory-simulated conditions equitable to different environments such as soil or seawater. However, unlike field tests, parameters such as temperature, pH, and humidity can be controlled and the number of measurable variables is larger and more precise than the field tests, including evolution of CO_2, analysis of residues and intermediates and oxygen consumption. In some occasions, to reduce or accelerate the time require for the analysis, nutrients are added to encourage growth of microorganisms. One of the examples for simulated test is soil burial test (explained below) or controlled composting test conducted by Pagga *et al* [89].

Soil burial test methods have been standardized for evaluating the degradability of plastics in the soil. The test material is buried in open field soil or in the tray containing soil under laboratory (greenhouse) conditions. In addition, this test can provide information on the degradation of plastics under specified conditions [92]. To minimize extrinsic variability and study the effects of a single factor by keeping the other variables constant, the greenhouse is considered a fitting environment. A main goal of the soil burial is to simulate to field conditions on a smaller, experimental scale, leading to benefits such as feasibility, reproducibility, and reliability [93].Soil burial studies are a major component of this dissertation.

2.5.5.3 LABORATORY TESTS

Laboratory tests, known for possessing high reproducibility, involve using the synthetic or defined media and inoculation of soil with mixed microbial population (e.g. from wastewater) or individual microbial community after screened for a particular polymer. The advantage of conducting lab test is optimizing the activity of particular microorganisms, which in turn, results in the higher degradation of polymer than under natural environment. This is helpful in studying the basic mechanism of polymer biodegradation but only limited conclusions on absolute degradation of plastics can be obtained [84].

2.6 COMPOSTABILITY AND COMPOSTING CONDITIONS OF PLASTICS

Compostability: According to ASTM sub-committee D20.96 and Standard guide D883, compostable plastic is defined as “a plastic undergoing biological degradation during composting to yield carbon dioxide, water, inorganic compounds, and biomass at a rate consistent with other known compostable materials and leaves no visually distinguishable or toxic residues (1996)”[94].

Composting conditions : Refers to a natural (biological) and aerobic process in which the organic materials such as manure, sludge, leaves, paper, and food waste are decomposed into a soil-like substance called humus (also known as compost). Decomposition is mainly carried out by microorganisms such as bacteria (mesophilic and thermophilic), and fungi. The organic matter serves as a food source for the microorganisms generating CO_2 and produce humus at the end of process. Compost is produced by either large-scale commercial (industrial) or a small-scale backyard (or home or farm) composting technique. Commercial composting is more effective and faster process than backyard composting. Commercial composting uses the mixture of manure, yard waste and food waste to produce the compost. A commercial composting facility uses heavy machine to turn and shred the wastes. In addition, high temperature ($>40^oC$), moisture levels, and aerobic microbial activity aid the multi-stage process to produce compost. In contrast, small-scale home composting, carried out in composting bins and small piles, requires temperature in the range of $10\text{-}40^oC$ to produce compost requiring
a longer time [15, 18, 85].

There are several deficiencies in the existing compostability standards and testing methods. A few of them are listed here.

- ***Duration of standards*** ASTM D6400 (9-12 months) and ASTM WK 29802 (24 months) are very long.
- ***A trained professional*** is always required to operate this instrument.

- ***Scarcity of the testing laboratories***: Currently, only 14 facilities are available throughout the world. In US, only two testing laboratories of them are available (Advanced Materials Center Inc. in Illinois and Organic Waste Systems in Ohio).
- ***Compost:*** Testing methods cannot be carried out with home compost or farm compost.
- ***Thick compostable materials*** (e.g. packaging material) cannot be tested using any of the test methods due to the limitations of test methods only to plastics [95, 96].

2.7 AMERICAN SOCIETY FOR TESTING AND MATERIALS (ASTM) INTERNATIONAL STANDARDS FOR BIODEGRADABILITY AND COMPOSTABILITY

ASTM International, a voluntary and non-profit Standardized organization, created a subcommittee under technical committee of degradable plastics (D20).The main goal of the subcommittee is develop and promote the standards. *A standard*, according to ASTM International, is a document that has been developed and established within the consensus principles of the society and meets the requirements of ASTM procedures and regulations. Six principal types of consensus standards are listed below:

1. *Standard Test Method* - a definitive procedure to identify, measure, and evaluate one or more qualities, characteristics, properties of a material, product, system, or service that produces a test result.
2. *Standard Practice* - a definitive procedure for performing one or more specific operations or functions.
3. *Standard Terminology* - a document consist of terms, definitions, description of terms, explanation of symbols, abbreviations, or acronyms.
4. *Standard Guide* - a series of general instructions or options that do not require a specific course of action.
5. *Standard Classification* - a systematic arrangement of materials, products, systems, or services into groups based on similar characteristics such as origin, composition, properties, or use.

6. *Standard Specification* - a precise statement and a procedure of a set of requirements comply by a material, product, system, or service [23].

2.7.1 ASTM STANDARDS FOR BIODEGRADABILITY OF PLASTICS

Although the development of standards is a painstaking process, it results in a standard possessing worldwide acceptance. Extensive works had been done in the past two decades to study and understand the behavior of biodegradable polymers in different environments (e.g. aqueous or marine, municipal sewage sludge) at composting conditions [90, 92, 97]. Various standards associated with biodegradability of standards utilize several testing methodologies; however, in-depth descriptions of biodegradability related standards and their testing methodologies are beyond the scope of this project and given elsewhere [95, 98]. ASTM standards and testing methodologies, pertinent to this project, are explained below.

2.7.1.1 ASTM STANDARD SPECIFICATION FOR BIODEGRADABILITY OF AGRICULTURAL PLASTICS IN SOIL (ASTM WK 29802)

The biodegradation of plastics in agricultural soil is the focus for this dissertation work. The biodegradation rate and percentage are higher under composting than at ambient soil conditions. Temperature does not increase to the thermophilic range in soil unlike what occurs in composting. Soil is considered as microorganisms-rich milieu than water due to high fungal activity in the former. The descending order of biodegradation activity of microorganisms in the different environments is as follows:

1. Compost (“Thermophilic trigger” with fungi and bacteria);
2. Soil (Fungi & bacteria);
3. Fresh water (bacteria);and
4. Marine water (dilute bacteria) [99].

Most agricultural products made with biodegradable polymers are not disposed via composting. After their useful lifetime, they often accumulate in soils. Standard test methods and specific criteria to verify biodegradability and absence of eco-toxicity are mandatory for biodegradable plastics in agriculture. Along the same lines, the following standard specification is proposed for the agricultural plastics biodegradable in soil.

ASTM WK 29802, *a standard specification for aerobically biodegradable plastics in soil environment*, encompasses the plastics used in the application such as erosion control, horticulture, and agriculture (e.g. mulch films). WK (work item) refers to a technical document in development stage, which will become a new standard or a revision to an existing standard. Some of the important technical specifications of this work item consist of:

1. Minimum biodegradation rate (conversion of carbon to CO_2) must be observed in the product after buried in the soil. This can be tested using the ASTM 5988, biodegradability test, or similar testing methods (explained in the Section 2.7.2.2) for 24 months.
2. Temperature should be within 20-28^{o}C (preferably 25 ± 2^{o}C) to simulate the conditions of cold and subtropical region.
3. The level of biodegradation will be determined for the whole material or for each of the organic constituents that occur at greater than 1% (by dry weight). The constituents that are lesser than 1% do not require separate testing; however, the concentration of constituents should not exceed more than 5% collectively.
4. Test products or the fragmented products formed after degradation should not adversely affect the soil ability to support plant growth—by comparing with blank that contain only soil. In addition, no acceptable levels of regulated metals or toxic materials are released into environment upon product decomposition.

According to ASTM WK 29802, all the materials should be crushed to powder for testing and be analyzed by a standard biodegradability test method, i.e., ASTM D5988. Some plastics undergo degradation only after the addition of specific additives. These plastics can be thermoformed with additives and tested for biodegradation using a standard test method. The nature, type and amount of additives should be reported because of the variability in the quality and quantity of the additives due to degradation. Brief descriptions about materials labeled as “biodegradable” according to this work item are as follows:

- *Class I. Plastics biodegradable in soil environment:* The “as-received” materials should be biodegradable in soil. These materials have tremendous horticultural or agricultural applications, and after or during the service life, these materials are buried in soil.
- *Class II. Plastics biodegradable in soil environment after environmental degradation:* Materials are biodegradable in soil only after undergoing environmental degradation for a reasonable length of time prior to soil burial. The products made of these plastics are wholly exposed to atmospheric factors; this exposure enables adequate biodegradability of materials after soil burial. Materials that are part exposed and part buried in soil should not be included in this class [100].

2.7.1.2 ASTM STANDARD SPECIFICATION FOR COMPOSTABLE PLASTICS (ASTM D 6400)

The ASTM D20 committee had developed standard ASTM D6400, “*Standard specifications for compostable plastics,”* in May 1999, to cover the products claiming to be compostable ASTM D6400 is proposed to establish the requirements for labeling materials and products, including packaging made from plastics, as “compostable in municipal and industrial composting facilities”. This standard determines if plastics and products are satisfactorily compostable and biodegradable at a rate compared to known compostable materials such as foodstuffs, lawn wastes, and paper. In addition, this standard specification requires degrading material should not diminish the value or utility of the compost resulting from the composting process. Three criteria of the standards are complete biodegradation, disintegration and environmental safety (Fig.11). The specifications, terminologies and guidelines for using the specific test methods are addressed in the standard ASTM D6400.This standard also encompasses three references of ASTM D20 documents for the testing and identification of materials. The important requirements of a plastic to be identified as “compostable” according to this specification are listed as follows:

1. *Disintegration during composting:* The plastic product should exhibit a considerable disintegration after 12 wk in a controlled composting test. This is examined by the retention of less than or equal to 10% of original dry weight of plastic product passed through a 2 mm sieve.
2. *Inherent biodegradation:* A plastic product must achieve biodegradation rate based on their composition where organic carbon is converted to CO_2 within the specified time. The requirement varies between polymer types.
    - ✓ *Homopolymers or random co-polymers*: 60 % of the organic carbon must be converted to carbon dioxide by the end of the test period when compared to the positive control.
    - ✓ *Plastic products containing more than one polymer of >1% concentration*: 60% of the organic carbon for each homopolymer must be converted to CO_2.
    - ✓ *Block co-polymers segmented co-polymers, polymer blends or low molecular additives*: 90% of the organic carbon is converted to CO_2 by the end of test period on comparing to positive control.
3. *Specified Time:* For testing non-radiolabeled plastics, the specified time is 180 days, whereas radiolabeled products should undergo testing for 365 days.
4. *Absence of eco-toxicity:* There should not be adverse effects on the ability of composts on plant growth—determined by phytotoxicity testing [98]— assessed by comparing the compost of positive control (cellulose) to the test material after discarded in the soil. Plastics or polymers, upon degradation, should not release any toxic substances in the environment [101].

Invoking this standard specification is warranted to identify the plastic as “compostable”. The complete list of testing methods from different standardization organizations of various countries to identify compostable materials is given elsewhere [95] and is beyond the scope of this dissertation.

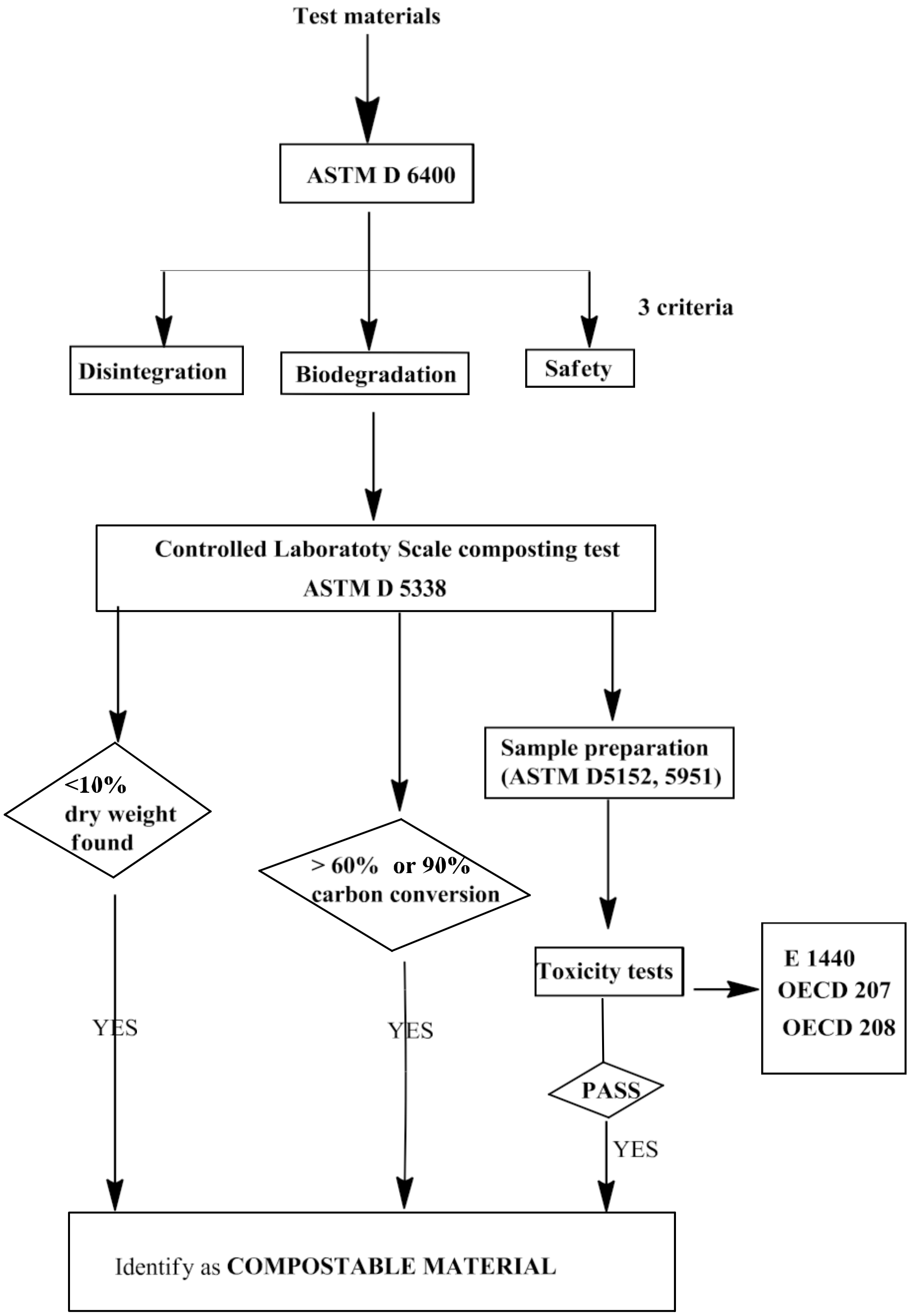


Figure 12: Compostable materials identification flow chart according to ASTM D6400 [95]

2.7.2 ASTM TESTING METHODS USED WITHIN THE STANDARD TO DETERMINE THE BIODEGRADABILITY OF PLASTICS IN SOIL

Standardization working groups agreed on two starting points that can be considered as building blocks for testing methods and definitions. They are:

- Test methods should generate reliable, quantitative, and reproducible results that evaluate biodegradability. This will allow transparency of the evaluation process and avoid claims based on qualitative data.
- Criteria and requirements should be formulated to prevent the accumulation of artificial products in soil, and ecotoxic effects.

The former starting point aims at unifying method and is the requirement of standardization, whereas the latter is based on the requirements by farmers, the public authority, and public opinion. Two important test methods (ASTM D5338 and D5988) prevailing in the biodegradable polymer industry to identify "biodegradable" plastics will now be explained. The key similarities and differences in the technical specifications of two test methods are briefly described.

2.7.2.1 STANDARD TEST METHOD FOR DETERMINING AEROBIC BIODEGRADATION OF PLASTIC MATERIALS OR RESIDUAL PLASTIC MATERIALS AFTER COMPOSTING IN SOIL (ASTM D5988)

The ASTM committee D20 developed ASTM D 5988-96/2003, "*Standard test method for determining aerobic biodegradation of plastic materials or residual plastic materials after composting in soil*", to test the products including formulation additives claiming to be biodegradable via composting. The plastic materials, not inhibitory to bacteria and fungi present in the soil, are tested. Brief details of technical specifications are:

1. Soils: Soil samples from three different locations are collected to maximize the biodiversity. The source of the soil samples should be reported. Soil is sieved to 2 mm particle size to remove plant materials, inert materials, and stones.
2. The source of inoculum is compost from municipal solid wastes (commercial compost).

3. In order to check the activity of soil, a reference material (i.e., starch or cellulose) known to fully biodegrade is used as positive control. If the theoretical evolution of CO_2 of the reference material is less than 70% in 6 months, then the test must be repeated with fresh soils and inoculum.
4. Temperature is kept in the range of 25 to 27^{o}C.
5. The presence of soil medium condition such as pH of 6-8 is necessary.
6. Moisture holding capacity (MHC) of soil should be 50-70% and soil moisture content, adjusted by adding distilled water, should be 80-100% of MHC ; and
7. Carbon and nitrogen ratio in soil is adjusted between 10:1 and 20:1 (by weight) through adding with ammonium phosphate solution.
8. Test material can be in the form of films, formed articles, dog bones, granules, and powder.

Results of this test method will determine the length of time plastics remain in the aerobic soil environment and degree of aerobic biodegradation of plastics by measuring the evolution of CO_2 as a function of time [102] [79].

2.7.2.2 STANDARD TEST METHOD FOR DETERMINING AEROBIC BIODEGRADATION OF PLASTIC MATERIALS UNDER CONTROLLED COMPOSTING CONDITIONS (ASTM D5338)

This is the test method for determining aerobic biodegradation of plastic materials under controlled industrial or municipal composting conditions. It determines the degree and rate of aerobic degradation of plastic materials at thermophilic temperatures. It requires mixing the plastic with stabilized and mature compost derived from the organic fraction of municipal solid wastes (inoculum). Temperature, aeration and humidity are monitored and controlled in the aerobic composting environment. Characteristic parameters of the technical specifications are:

1. Cellulose is used as a positive control, whereas PE often serves as negative control. A blank containing only inoculum or compost is used in this test method. If the minimum of 70% biodegradation (conversion of carbon to CO_2) is not

observed for positive control in 45 days, then the test must be repeated with new compost.

2. Temperature is held in the range of 58-60°C.
3. Carbon and nitrogen ratio should be between 10 and 40 of both the test and inoculum (compost) combined.

The percentage of biodegradation is obtained from the ratio of average net CO_2 production of test materials to original carbon content of test materials (determined by elemental analysis). In addition to carbon conversion, disintegration (by visual interpretation) and weight loss can also be evaluated [95, 103].

2.8 SOIL BURIAL STUDY 1

2.8.1 OVERVIEW OF EXPERIMENTAL DESIGN

Wadsworth *et al* [12] conducted this soil burial study for 30 wk from March 2010 to October 2010, prior to my participation in this research project [12]. There were three soil amendments—a control containing only high tunnel (HT) soil (Dewey silt loam soil from USDA certified organic farm), HT soil with lime, and HT soil with compost. Statistical experimental design of completely randomized with two retrieval times of 10 and 30 wk and three mulches with three replicates—cellulose, meltblown (MB)-PLA, and spunbond (SB) -PLA-2010. Three experimental factors—burial time, mulch type, and soil amendment—were investigated to determine the significance in changes of physio-chemical parameters such as tensile strength or breaking load (N), breaking elongation (%), air permeability ($cm^3/g/cm^2$), weight (g/m^2), thickness (mm), number-averaged molecular weight (M_n) (g/mol) and polydispersity index (PDI) and fiber breakage via scanning electron microscopy (SEM). A description of the "as-received mulches" used in this study is as follows:

- *WeedGuardPlus®:* A brown cellulosic product, with weight of 107 g/m^2, was obtained from Sunshine Paper Co. LLC, Aurora, CO, USA. The flat and ribbon-like shape fiber, of diameter ~ 21 microns observed by scanning electron microscopy (SEM), is one factor distinguishing cellulosic mulch from SB and MB nonwoven. The inherent characteristics of cellulosic mulch were higher fiber diameter (μm) and tensile strength (N) and lowest breaking elongation (%).

- *Spunbond (SB-PLA-2010) and MB nonwoven:* SB and MB nonwoven were prepared under supervision of Dr. Larry C. Wadsworth. The MB PLA was produced at a specified weight of 80 g/m^2 and width of 0.32 m by Biax-Fiberfilm Corporation, Greenville, WI, USA from a blends of 80% Ingeo 6201D PLA (Melt Index (M.I) of 15-30) and 20% Ingeo PLA 3251D (M.I of 70-85) with both PLA grades obtained from NatureWorks. Fiber diameters of SB and MB mulches were measured to be 15.0 and 6.3 microns, respectively (SEM analysis). Tensile strength value of "as-received" SB-PLA-2010 and MB-PLA were 9.0 N and 7.0 N, respectively.

2.8.2 RESULTS AND DISCUSSION

2.8.2.1 EFFECT OF SOIL AMENDMENTS ON MULCHES

The effect of soil amendments is discussed below except for the cellulosic mulch. Cellulose underwent complete disintegration before 10 wk under all the soil amendments; therefore, it could not undergo physico-chemical analysis. There were no considerable changes in PDI values of SB and MB nonwoven mulches in all the soil amendments. In addition, there was no fiber breakage observed in SB nonwoven mulches due to soil amendments (SEM analysis), explaining their durability in the soil. In contrast to SB nonwoven mulches, there was significant deterioration indicated by the apparent fiber breakage.

2.8.2.1.1 NO AMENDMENTS (CONTROL)

For SB-PLA-2010, there was an insignificant change in the value of breaking load, or tensile strength, after 10 wk; however, after 30 wk, the value decreased from 8.9 to 2.3 N. The M_n of SB-PLA-2010 underwent 4.5% decrease after 30 wk in high tunnel soil. The tensile strength value of MB-PLA decreased from 6.8N to 2.2N after 10 wk. Because of extreme deterioration, the tensile strength testing was not performed on MB-PLA for 30 wk. The loss of M_n for MB-PLA was only 5% after 30wk.

2.8.2.1.2 HIGH TUNNEL SOIL TREATED WITH LIME:

The tensile strength loss of MB-PLA after 10 wk was the highest among the mulches treated with lime (86.5%). The M_n loss of MB-PLA, buried in high tunnel soil and treated with lime, after 10 wk was negligibly small (< 1%); after 30 wk, the loss was 4.4 %. However, the M_n loss of MB-PLA after 30 wk, although larger than at 10 wk, was almost similar to the control (4.8%). There was insignificant decrease of tensile strength value for SB-PLA-2010 after 10 wk. After 30 wk, the tensile strength value of SB-PLA-2010 decreased by 83%, an higher extent compared to control (70%).The M_n decreased from 135,000 (g/mol) to 134,000 and 130,000 (g/mol) after 10 and 30 wk, respectively. The loss of M_n for SB-PLA-2010 after 30 wk was slightly lower (3.3%) than control (4.8%).

2.8.2.1.3 HIGH TUNNEL SOIL TREATED WITH COMPOST:

In the presence of compost, SB-PLA-2010 underwent a ~1.7% decrease of M_n after 30 wk. The M_n loss was lower than control (4.8%) and lime amendment (3.3%). The extent of loss of tensile strength for SB-PLA-2010 under compost amendment after 30 wk was similar (~2.2N) to control and lime amendment. The M_n of MB-PLA decreased from 118,000 to 113,000 g/mol after 30 wk—the depolymerization of MB-PLA in compost was similar to control and lime amendment. The tensile strength value decreased by 86% after 10 wk, to the similar extent as lime amendment (86%) ; however, it was higher than control (70%).

2.8.3 SUMMARY

The extent of depolymerization was minor for both of the nonwoven mulches—determined from observing the decrease of M_n. The weakening of fibers determined from loss of tensile strength value, due to lime and compost amendments, was higher (86.6%) for MB-PLA than SB-PLA (76%). MB-PLA, employed in this soil burial study, was not used in this dissertation. A lower molecular weight feedstock was employed to prepare MB-PLA herein. Among the variables determined in this study, air permeability, weight, and thickness of all mulches were not employed in this dissertation. The adherence of soil particles to the mulches and difficulty in the subsequent removal led to a decrease of air permeability and increase of weight and thickness, which are opposite trends than those expected for biodegradation. In general, the emphasis of soil burial study is on the first stage of degradation for PLA-based nonwoven, in accordance with hypothesis, under aerobic conditions (Section 2.5.3). Based on results of this preliminary research, the blueprint for upcoming soil burial studies was drawn by my dissertation advisors and I with additional tests included such as monitoring the environmental conditions for biodegradability [12].

2.9 CONCLUSIONS

In this chapter, a literature review regarding PLA, PLA/PHA blends, PLA nonwoven processing, SB and MB nonwoven, and standards and testing methods to examine the biodegradability of plastics, including important definitions pertinent to this dissertation, were discussed in detail. The focus of the review was to provide the frame of reference for upcoming chapters in this dissertation.

Although ASTM WK 29802 is an appropriate proposed standard for this dissertation, it is still under revision and yet to be officially accepted. In addition, both the standards ASTM WK 29802 and D6400 require a testing method to addresses the rate and extent of biodegradability. Nonwoven, with high mechanical strength and higher surface area (due to smaller fiber size) leading to enhanced hydrolysis, are considered as potentially valuable agricultural mulches with several advantages over currently available BDMs:

- There are no pure starch-based thermoplastic polymers per se. A few commercial starch-based polymers are blends and graft copolymers between starch and caprolactone or starch and vinyl acetate (e.g. Novamont’s Mater-Bi™ grades)[71].
- A lack of mechanical strength and the occurrence of preharvest biodegradation make Mater-Bi™ are major disadvantage for several of the currently available BDMs.

- Among the partially biobased plastics, a satisfactory rate of biodegradation at ambient soil conditions was reported only for Mater-Bi™ [79]. Although Mugnozza *et al* suggested the burial of the spongy residual material remaining after the biodegradation of Mater-Bi™ in soil [104], the composition and ultimate fate of that material are still unknown.
- Besides, Mater-Bi™ (starch-based mulch) and Ecoflex (PBAT-based mulch) are partially fossil fuel-biobased.
- The rate and degree of biodegradation of other commercial BDMs under ambient soil conditions remains equivocal. For instance, biodegradability of Ecoflex™ (PBAT) after UV and sunlight exposure had decreased due to cross-linking; the rate of biodegradation of cellulose acetate, used as films, depends on degree of substitution of acetyl groups [105, 106].
- A large quantity of PLA is produced by NatureWorks LLC—located in Blair, Nebraska with a production capacity of 140,000 tonnes of lactic acid per year. The cost of PLA is relatively less compared to other biopolymers and conventional plastics; for instance, PLA is 2.1 USD per kg [107], whereas PHA, starch and its blends, and PCL cost 7-20 USD/kg, 5.2 USD/kg and 6.9 USD/kg [108], respectively. The costs of polypropylene and polystyrene are 2.1 and 2.2 per kg [107], respectively. Thus, the cost of PLA is nominal and comparable to petroleum-based polymers. In addition, nearly 800,000 metric tonnes of PLA will be produced worldwide by 2020 that may reduce the cost further. This will ensue to replace petroleum-based polymers with PLA in all the agricultural applications.

In this dissertation, PLA and PLA/PHA blends nonwoven were prepared and tested for biodegradability by soil burial studies under the greenhouse conditions simulating the field test. Temperature, pH, and soil moisture were continuously monitored and recorded. Results from the Studies, given in Chapters 3-7, provide an insight about the fragmentation and biodegradability of PLA nonwoven mulches. In addition, the ASTM

D5388 testing method, after simulated weathering, was used to evaluate the biodegradability of weathered vs. “as-received” PLA nonwoven mulches (Chapter 8).

CHAPTER 3

SOIL BURIAL STUDY 2: EFFECT OF SOIL MOISTURE AND AMENDMENTS ON THE BIODEGRADATION OF PLA- AND PLA/PHA BLENDS -BASED NONWOVEN MULCHES

3.1. INTRODUCTION

Although polylactic acid (PLA) is a biobased and compostable polymer, the biodegradation under ambient soil condition is rather slow [109-112]. Possible avenues to enhance the biodegradation of PLA are by the addition of an enzyme, such as bromelain, and either by copolymerization or blending with a plasticizer or another polymer, such as polyhydroxyalkanoate (PHA), that decreases the crystallinity of PLA. The biodegradation of PLA by bromelain, a member of the protease family of enzymes, was first reported by Williams [113] in 1981. It is hypothesized that the PLA nonwoven mulches will undergo degradation by administering pineapple juice (PJ)—a significant source of bromelain and an additional source of carbon-energy to microorganisms.

Soil moisture is a critical biotic factor, which needs to be at the optimum level (20-40%) [114] . Moisture, generally, impacts the chemical properties of soil such as redox potential, pH, O_2 and CO_2 levels, which in turn often enhances the microbial activity in soil [115]. The delivery of tap water to the soil serves as a source of nutrients (e.g., magnesium and calcium dissolved in water) to microorganisms, in addition to supplying hydrogen and oxygen. Moreover, addition of water also transports food nutrients to soil microorganisms [116]. Water delivery rates in Study 2 more or less simulate the organic field irrigation conditions and serve as soil amendments in investigating the biodegradation of PLA and PLA/PHA blends nonwoven mulches.

To enhance the biodegradability of PLA from that observed in Study 1(Section 2.8), new SB and MB mulches were prepared from lower molecular weight PLA and PLA/PHA blends nonwoven mulches. A main goal of Study 2 is to test the biodegradability of the new SB and MB mulches, as a function of water delivery rate and the addition of PJ, a carbon source for microorganisms and a possible source of bromelain. A hypothesis that the addition of PHA will enhance biodegradation of PLA based nonwoven mulches under ambient soil conditions, using soil enriched with compost is also tested. Study 1 demonstrated that compost was one of the effective amendments—the underlying reason for using soil mixed with compost.

3.2. OBJECTIVES

The aim of Study 2 was to assess and understand the effect of PJ—a carbon-energy source for microorganisms and a source of enzyme (bromelain)—on the biodegradation for PLA and PLA/PHA blends based nonwoven mulches. The influence of the presence and absence of PJ—in conjunction with the two levels [high and low] of water delivery rate—on biodegradation of nonwoven mulches was determined. In addition, the biodegradability of PLA was compared to PLA/PHA blends for all the soil amendments. The PLA and PLA/PHA blends nonwoven mulches retrieved from 10 and 30 wk of soil burial were assessed, and the results are reported.

3.3. EXPERIMENTAL

3.3.1. MATERIALS

Pineapple juice (PJ) was obtained commercially from local grocery store. The soil (Dewey silt Loam) for all four treatments was collected from a USDA certified organic farm. Black Kow® Compost was purchased from Oxford, FL, USA. All the nonwoven mulches employed in Study 2 were prepared under the supervision of Dr. Larry C. Wadsworth, Professor Emeritus, Material Science and Engineering Dept., UTK. PLA feedstock was obtained from NatureWorks, LLC, Blair, NE, USA. PHA feedstock was obtained from GreenBio Corporation, Tianjin, China (Section 1.3.2). The latter's molecular structure was provided in Fig.6. Spunbond (SB) and meltblown (MB) mulches were prepared at Saxon Textile Research Institute (STFI), Chemnitz, Germany, and Biax-Fiberfilm Corporation Greenville, WI, USA, respectively. The inherent physico-chemical properties and feedstock of mulches used Study 2 is given in Table 4.

3.3.2. EXPERIMENTAL DESIGN

The statistical experimental design for Study 2 was randomized complete block (RBD), blocked on mulches. The amount of PJ was modified (3 ml to 30 ml) from the preliminary study. There were four soil treatments applied to each of the four mulches and were applied via trickling using a watering can every 48 hr for 10 or 30 wk.

- High (tap) water delivery rate (HWDR) with pineapple juice (PJ) (1000 mL of water + 30 mL of PJ);
- Low water delivery rate (LWDR) with PJ (500 mL of water + 30 mL of PJ);
- High water delivery rate (HWDR) (1000 mL); and
- Low water delivery rate (LWDR) (500 mL).

Table 4: Inherent physico-chemical properties of PLA-based nonwoven mulches with feedstock, used in Study 2

Mulch[a]	Feedstock[b]	Color	Weight[c] (g/m^2)	Fiber diameter[d] (µm)	Thickness[d] (µm)	M_n[e] (kDa)	Tensile strength[d,f] (N)
SB-PLA-2011	Ingeo® 6252D (PLA)+ 1-2% Carbon black	Black	82.4±6.4	15.8±0.5	660±27	101±1.9	37.12±3.84
MB-PLA	Ingeo® 6252D (PLA)	White[g]	79.1±2.8	7.5±0.6	483±19	99.5±1.7	8.96±2.23
MB-PLA+PHA-85/15	Ingeo® 6252D (PLA) + Greenbio (PHA)	White[g]	90.5±1.4	14.2±1.0	717±46	89.9±0.4	1.48±0.58
MB-PLA+PHA-75/25	Ingeo® 6252D (PLA) + Greenbio (PHA)	White[g]	84.2±4.1	15.3±0.6	593±40	75.8±0.6	3.90±0.09

[a] All the mulches were prepared in 2011.MB,SB and PHA refer to meltblown,spunbond and polyhydroxy alkanoate, respectively with weight percent of PLA and PHA given in mulch name;[b] Ingeo® are PLA products obtained from NatureWorks, Blair, NE USA (melt indices for 6252D and 6202D are 70-85 g per 10 min and 15-30 g per 10 min, respectively. Ingeo® 6252D and 6251D are identical, except for the inclusion of a biodegradable pellet lubricant for the former), PHA obtained from GreenBio (Tianjin, China);[c] Uncertainty values reflect standard deviation ; [d] Uncertainty values reflect standard error ; [e] Number-averaged molecular weight of PLA component based on polystyrene standards with standard error; [f] Tensile strength of nonwoven mulches ; [g] Natural color of the nonwoven and no titania added.

There were two replicates for each combination of treatments, mulch and burial time. Mulches were retrieved at two time intervals (10 and 30 wk); thus the total number of experimental trays was 64 (4 * 4 * 2 * 2). The experiment, conducted in Greenhouse 16 on the UTIA campus, was started on August 29, 2011. The 30 wk samples were retrieved on March 21, 2012. Air and soil temperatures were monitored—using Waterscout SM 100 sensors purchased from Spectrum Technologies, Plainfield, IL ,USA—and reported to be 23.9± 3.4°C and 15.6±5.6°C, respectively. Moisture levels for HWDR and LWDR treatment were 31.9 ±18.5% and 37.4± 3.6% throughout Study 2, respectively. The soil-compost filled trays that received low water delivery rate treatment were saturated with water; hence, the soil moisture values between HWDR and LWDR did not differ ($p>0.10$).

3.3.3. MULCH BURIAL, RETRIEVAL, AND CLEANING AFTER THE EXPERIMENT

The mulches were buried in plastic trays measuring 52 cm length x 25 cm width x 6 cm deep (Fig.13). The tray contained a mixture of 7500 g of soil and 585 g of compost. The trays underwent hand-weeding on a daily basis for one week prior to burial of the mulches to minimize the occurrence of weeds during the experiment. Only one mulch sample of size 61 cm x 38 cm was buried in each tray, 2 cm beneath the top layer of soil. Buried mulch specimens were carefully removed from the trays, cleaned with water after being sandwiched between the two layers of nylon organza (Fig.14). The specimens were air-dried for two days according to standard textile conditions and tested for physico-chemical properties described below.

Figure 13: Plastic trays containing mulches buried in soil and compost mixture arranged in randomized block experimental design with the experiments conducted in a greenhouse (Study 2)

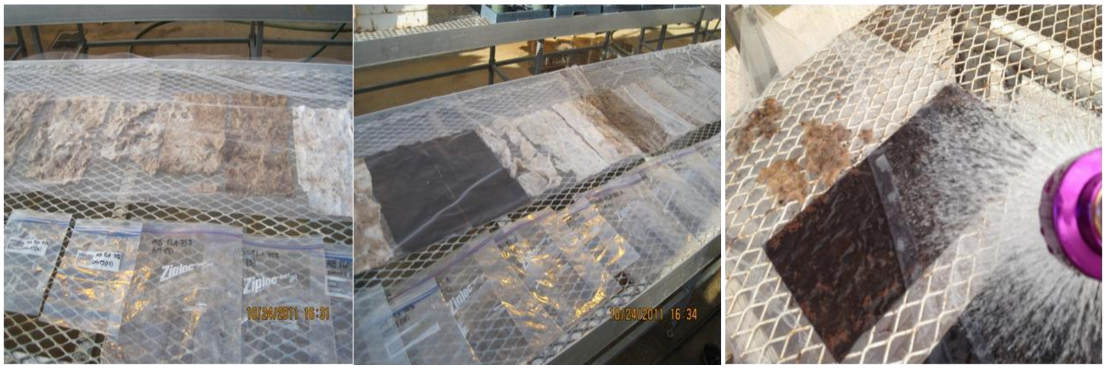


Figure 14: Mulch cleaning after 10 & 30 wk retrieval from Study 2

3.3.4. PHYSICO-CHEMICAL ANALYSIS OF MULCHES: EXPERIMENTAL METHODS

Table 5 provides the list of analyses used for the characterization of biodegradation of mulches for this dissertation. Almost all of the methods, except tensile strength testing, were employed on mulches retrieved from soil after 30 wk.

Table 5: Overview of methodology for evaluating mulches retrieved from soil for Studies 2-6

Experimental method	Information obtained	Burial Time applied (wk)[d]
Tensile strength testing	Decrease in tensile strength	10 and 30[c]
Gel permeation chromatography (GPC)	Decrease in number-average molecular weight (M_n) in and increase in polydispersity index (PDI)	10 and 30
Fourier transform infra-red spectroscopy (FTIR)	Determine the occurrence of random chain scission as well as hydrolysis of ester bonds	30
Scanning electron microscopy (SEM)	Visualization of microscopic fiber bond breakage and the measurement of average fiber diameter[a]	30
Differential scanning calorimetry (DSC)	Changes in thermal properties such as T_g, T_m, ΔH_m, T_c and ΔH_c[b]	10 and 30

[a] Using the software, ImageJ ; [b] T_m-Melting temperature, ΔH_m-Enthalpy of fusion, T_c-Crystallization temperature ,T_g- Glass transition temperature , ΔH_c-Enthalpy of crystallization ; [c] MB nonwoven mulches were not analyzed after 30 wk because of extreme deterioration ;[d] Study 4 was conducted only for 10 wk.

3.3.4.1. TENSILE STRENGTH TESTING

The maximum force applied to a material to rupture is called the breaking load, breaking force or tensile strength. Materials that are brittle rupture at the maximum force, whereas materials that are ductile usually experience a maximum force before rupture [117]. Pure PLA has a tensile strength value of 62.7 MPa [118]. A polymeric compound becoming brittle during a low or high temperature exposure or as a result of ageing is called embrittlement [119].

Tensile strength testing followed ASTM D 5035-11[120] .The cut-strip approach of this ASTM testing method is commonly used for nonwoven textiles to determine the tensile strength (N) and elongation at breakage (%)[12]. SB samples were cut into 4-8 subsamples in the machine direction of size 2.54 cm *15.24 cm, whereas all of the MB-PLA specimen was in 2.54 cm *10.16 cm and analyzed for tensile strength. The difference in the length of the MB and SB subsamples was due to considerable deterioration of the former samples after 10 wk. The gauge length for SB samples was 7.62 cm and 2.54 cm for all MB samples. The strips were tested by extending the samples at a failure rate of 30.48 cm per minute. Experiments were carried out with a United Testing systems (UTS model SFM-20 load frame, load cell: 10 kN, United Calibration Corporation, Huntington Beach, CA, USA) at 25 °C.

3.3.4.2. GEL PERMEATION CHROMATOGRAPHY (GPC)

A separation technique in which separation mainly according to the hydrodynamic volume of the molecules or particles takes place in porous non-adsorbing material with pore size as same as the effective dimensions in solution of the molecules to be separated. This is accomplished by injecting a small amount (300-400 µl) of polymer-dissolved solvent into column(s) containing porous beads. Smaller molecules enter into porous beads and reside for greater length of time compared to larger molecules. The number-averaged molecular weight (M_n), weight-averaged molecular weight (M_w) and polydispersity index (PDI-ratio of M_w to M_n) are calculated from the analysis.

At least two chromatographic analyses were employed for mulch retrieved from a given experimental tray. Mulch samples (~ 20 mg) were dissolved in 5 mL of chloroform and stirred for 1 h. The samples were then centrifuged at 10,000 rpm (6149 g) for 1 min, and passed through 0.20 µm nylon filters to remove insoluble soil particles that adsorbed onto the mulches. The filtered solution (300 µL) was injected into a dual-pump HPLC system (Varian, Walnut Grove, CA USA) equipped with model Mark III evaporative light scattering detector (WR Grace, Deerfield, IL USA), a 300 x 7.5 mm column(ID PL Gel mixed D) purchased from Agilent, Santa Clara, CA USA. Chloroform was employed as mobile phase at a flow rate of 0.8 mL/min. Molecular weight values are reported as polystyrene molecular weight equivalents, using EasiVial PS-H polystyrene standards from Agilent.

3.3.4.3. DIFFERENTIAL SCANNING CALORIMETRY (DSC)

DSC is an analytical technique that measures the heat flow rate to or from a sample specimen as it is subjected to a controlled temperature program in a controlled atmosphere. This instrument is used to measure the following parameters.

a. Glass transition temperature (T_g): Defined as the reversible transition in amorphous materials (or in amorphous regions within semi crystalline materials) from a hard and relatively brittle state into a molten or rubber-like state [121].

b. Melting temperature (T_m) or melting point: A transition from a crystalline or semi-crystalline phase to a solid amorphous phase is defined as melting temperature or melting point. In general, $T_m > T_g$ [122].

c. Enthalpy of fusion (ΔH_m): the amount of heat per unit mass needed to change a substance from a solid to a liquid at its melting point. Heat of fusion = heat added/ mass of material

d. Crystallization temperature (T_c): An exothermic event where a liquid changes to a solid and is depicted as a peak.

e. Enthalpy of crystallization (ΔH_c): The heat energy released upon crystallization is called enthalpy of crystallization.

f. Crystallinity: Refers to the orientation of disordered long polymer chain molecules into a repeating pattern, which affects stiffness, hardness, flexibility, and heat resistance [32].

DSC was carried out for SB and MB mulches before and after soil burial (30 wk burial time) but only for one of the two replicates, using a model Q20 calorimeter from TA Instruments (New Castle, Delaware, USA). The following temperature programming was employed for mulch samples (~5-10 mg and 2-5 mg for SB and MB mulches, respectively): heating at 10^oC min^{-1} from 40^oC to 200^oC; temperature held constant at 200^oC for 5 min; followed by cooling at 10^oC min^{-1} until reaching -50^oC. The temperature was held at -50^oC for 5 min. Subsequently, a second heating-cooling cycle was employed using the same conditions as the first cycle, as given above. From the thermograms, T_g, T_c and the enthalpy of crystallization (ΔH_c) were determined from the second heating cycle for PLA, and the temperature of melting, or fusion (T_m) and the enthalpy of melting or fusion (ΔH_m) were determined via the first heating cycle, for both PLA and PHA. T_c and ΔH_c of the PHA component in PLA/PHA blends were not determined due to thermal degradation at $>200^oC$ in the first heating cycle, leading to the absence of a peak for crystallization for the second cycle. , leading to the absence of a peak for crystallization for the second cycle.

Fig.15 shows the representative thermogram of “as-received” MB-PLA+PHA-75/25 of two thermal scans. T_m, peak temperature and ΔH_m were determined from the DSC endotherm; T_g was determined from midpoint of heat capacity change. The peak crystallization temperature, T_c, was corrected using indium standard and ΔH_c was determined from exotherm.

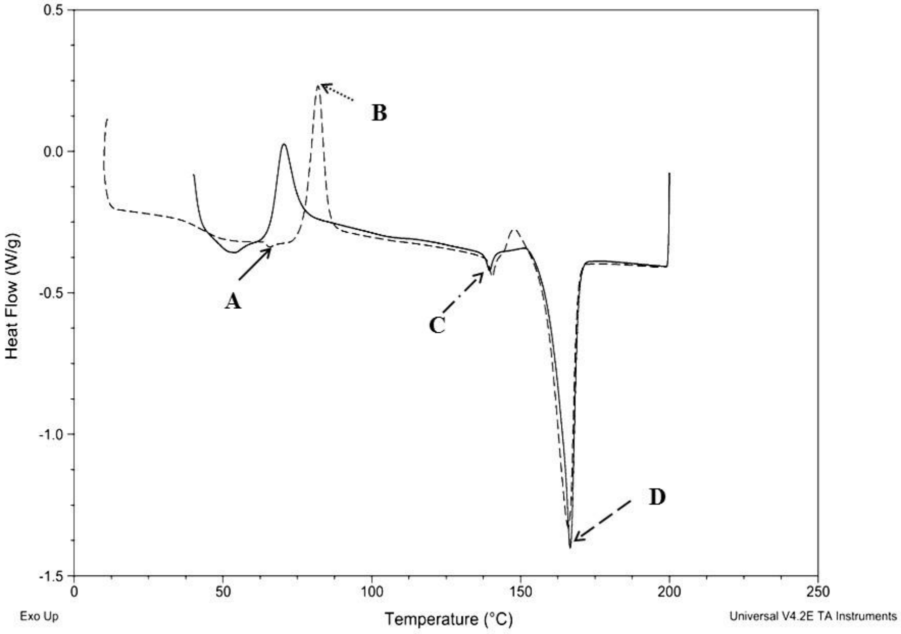


Figure 15: DSC thermograms of "as-received" MB-PLA+PHA-75/25 ; Solid line (------) represents the first thermal scan and dashed line (- - - -) represents the second thermal scan. "A" and "B" peak point in the second thermal cycle represents the glass transition temperature and crystallization temperature, respectively. "C" and "D" peak point represented the melting temperature of PHA and PLA, respectively.

The percentage (or degree) of crystallinity of the PLA component of the nonwoven mulches, X_c, is determined from the following equation [123]:

$$\boldsymbol{X_c = \frac{\Delta H_m - \Delta H_c}{\Delta H_{m^0}} * 100} \ \% \qquad (\mathbf{3})$$

where ΔH_{m0} is the melting enthalpy of 100% crystalline PLA sample and value of this constant is 93.6 (J/g), ΔH_m and ΔH_c are enthalpy of melting and crystallization, respectively.

3.3.4.4. SCANNING ELECTRON MICROSCOPY (SEM)

An electron microscope is used to scan the surface of material using the beam for focused electrons; these electrons are reflected back to form an image. The electrons of light interact with electrons on the surface of sample and create signals that are detected and the surface topography is interpreted.

Mulch samples obtained at the beginning and end of soil burial (30 wk, for one of the replicates) were mounted on a 1.2 cm diameter aluminum disk using double side adhesive carbon tape. Then the subsample was sputter-coated with a thin layer of gold (less than 5 nm) in a vacuum chamber using argon gas and a small electric current of approximately 3 mA. Digital photomicrographs were made at 100,500 and 1000X with a LEO 1525 field emission scanning electron microscope (Zeiss, Oberkochen Germany), in the MSE Department at UTK.

3.3.4.5. FOURIER TRANSFORM INFRA-RED SPECTROSCOPY USING ATTENUATED TOTAL REFLECTANCE (FTIR-ATR)

Fourier transform infra-red spectroscopy (FTIR) is a technique which is used to obtain an infrared spectrum of absorption, emission, photoconductivity or Raman scattering of a solid, liquid or gas. The spectral data is collected in a wide spectral range [124]. A qualitative surface analysis is provided by attenuated reflectance infrared spectroscopy (FTIR-ATR). The characteristic wavenumber for the specific bonds can be obtained from elsewhere [123, 125].

FTIR-ATR was employed only for the initial mulches and mulches retrieved after 30 wk of soil burial. FTIR spectroscopy was completed using the Spectrum One FTIR spectrometer from Perkin Elmer (Waltham, MA, USA) with a diamond attenuated total reflectance (ATR) attachment. Spectra were collected over the range of 4000-600 cm^{-1} in absorbance mode with 1 cm^{-1} resolution and eight scans per spectrum. Ten spectra were collected for all mulches retrieved from the experimental soil trays (after being cleaned as described above) and were transformed by reducing the spectral resolution to 4 cm^{-1} , and normalized in the Spectrum software (v. 10.04). Spectra reported herein reflect the average of data collected from mulches retrieved from two replicate trays. FTIR-ATR data for this soil burial study was collected by Ms. Rachel N. Dunlap, an undergraduate Research Associate.

3.3.4.6. SOIL pH AND BROMELAIN ACTIVITY ASSAY

Soil pH tests were performed on soil samples treated with PJ or its absence and /or high or low water delivery rate for two wk period at the Soils and Plant Analysis Laboratory of University of Tennessee, Nashville, TN, USA. The 1:1 water method was used and inductively coupled plasma mass spectrometry (ICP-MS) as part of the Mehlich 1 soil extraction method respectively, upon 100-150 g soil samples. Measurements for soil pH and calcium and magnesium levels are within 0.1 pH units and 5.6 g m^{-2}, respectively. Replicate measurements were taken for untreated soil to determine the uncertainty between soil samples of a given treatment. The activity of hydrolytic enzymes (bromelain) present in PJ was measured through an activity assay based on the hydrolysis of gelatin digestion method [126].

3.3.4.7. STATISTICAL METHODS

Analysis of variance (ANOVA) was conducted using mixed model in SAS 2013, V9.3, SAS Institute Inc., Cary, NC, USA. Mean values were calculated and compared using Fisher's Least Significance Difference method.

3.4. RESULTS

3.4.1. EFFECT OF PJ AND WATER DELIVERY RATES ON SOIL PROPERTIES

Study 2 investigated the effect of two different levels of water delivery rate and the absence versus presence of PJ administered to the mulches buried in the soil and compost-filled trays. The activity level of the hydrolytic enzyme "bromelain" in PJ was insignificant– as determined from an activity assay [126]. However, PJ is considered as a valuable amendment as the carbon source of PJ might have increased microbial abundances in the soil. The weed growth, intriguingly, was suppressed by PJ addition. The soil properties, particularly pH, were not changed extensively due to PJ addition (Table 6).

The average soil moisture obtained using the two different delivery rates were not significantly different; this suggested that soil under both conditions was saturated with water. Tap water, administered as the high and low water delivery rate treatment, possessed a considerable amount of calcium and magnesium accounting for increased levels in soils relative to untreated soils.

Table 6: Comparison of soil properties after two wk of treatment

Treatment	**Soil pH**	**P[a]**	**K[a]**	**Ca[a]**	**Mg[a]**
Untreated	6.2	92.0	456.6	403.3	685.4
LWDR+PJ[b]	6.5	82.4	551.0	4196.1	701.2
HWDR +PJ[c]	6.4	64.2	626.1	3279.4	667.3
LWDR[d]	6.8	273.7	1071.7	6700.5	1017.2
HWDR[e]	6.6	92.0	605.5	3526.4	639.4

[a]All the nutrients are in kilogram per hectare ; [b] Low water delivery rate and 30 mL of pineapple juice ; [c] High water delivery rate and 30 mL of pineapple juice; [d] Low water delivery rate ; [e] High water delivery rate

3.4.2. VISUAL OBSERVATION OF NONWOVEN MULCHES BEFORE AND AFTER BURIAL IN SOIL

Visual observations of mulches at different retrieval times (0, 10, and 30 wk) are depicted in Figs.16-18. Mulches displayed in these figures are for PJ and water delivery rates that led to greatest loss of M_n. Significant deterioration was observed for MB-PLA (Fig.16), MB-PLA+PHA- 75/25 (Fig.17), and MB-PLA+PHA-85/15 (not shown) after 30 wk. As a result, MB nonwoven mulches were not tested for the tensile strength after 30 wk. As shown in Fig 18, SB-PLA-2011 remained intact after 10 and 30 wk for all treatments.

Figure 16: Visual observation of MB-PLA retrieved from burial in soil (Study 2) treated with LWDR+PJ at 0, 10,and 30 wk (left to right).

Figure 17: Visual observation of MB-PLA+PHA-75/25 retrieved from burial in soil (Study 2) treated with HWDR + PJ at 0, 10, and 30 wk (left to right).

Figure 18: Visual observation of SB-PLA-2011(black) retrieved from burial in soil (Study 2) treated with LWDR + PJ at 0, 10, and 30 wk (left to right)

3.4.3. CHANGE OF TENSILE STRENGTH FOR NONWOVEN MULCHES

In general, trends involving the tensile strength values mirror those described above from the visual observation. The following comparisons and inferences were made between as-received and 10 wk retrieved MB nonwoven mulches, based on the change of tensile strength encountered for each mulch (Fig.19). Mixed model of analysis was performed, in SAS (9.3) software, independently for MB- and SB-PLA because all MB mulches underwent complete disintegration after 30 wk. The soil amendments did not affect the loss of tensile strength of MB-PLA and MB-PLA+PHA blends (75/25 and 85/15) significantly (p= 0.42) as determined from ANOVA. The loss of tensile strength for all PJ treated MB mulches were 77-78%, while the both levels of water delivery rate treated MB mulches (in the absence of PJ) underwent 85-90% loss of tensile strength value. Embrittlement and fragmentation of all the MB mulches prevented tensile strength testing at 30 wk. Statistics of tensile strength for SB-PLA-2011 was determined independently owing to the tensile strength testing performed after 30 wk retrieval time for each treatments. The loss of tensile strength for SB-PLA-2011 after 30 wk was not affected significantly by any of the soil amendments employed in Study 2 (Fig.20,p=0.17) . Thus, SB-PLA-2011 was refractory to all the soil amendments with respect to the loss of tensile strength.

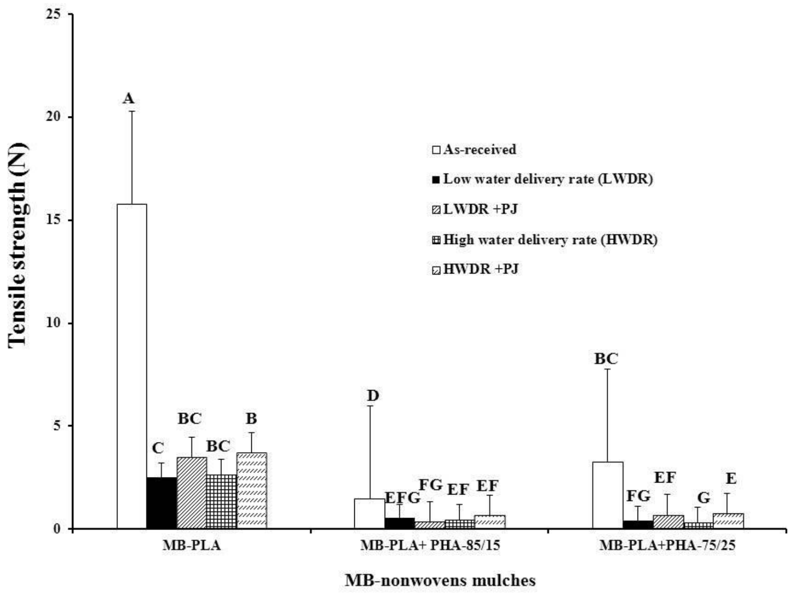


Figure 19: Comparison of tensile strength values of all MB nonwoven mulches retrieved after 10 wk in Study 2. Mean values (represented by grouped bars) with no common letter groupings are statistically different (p<0.05).

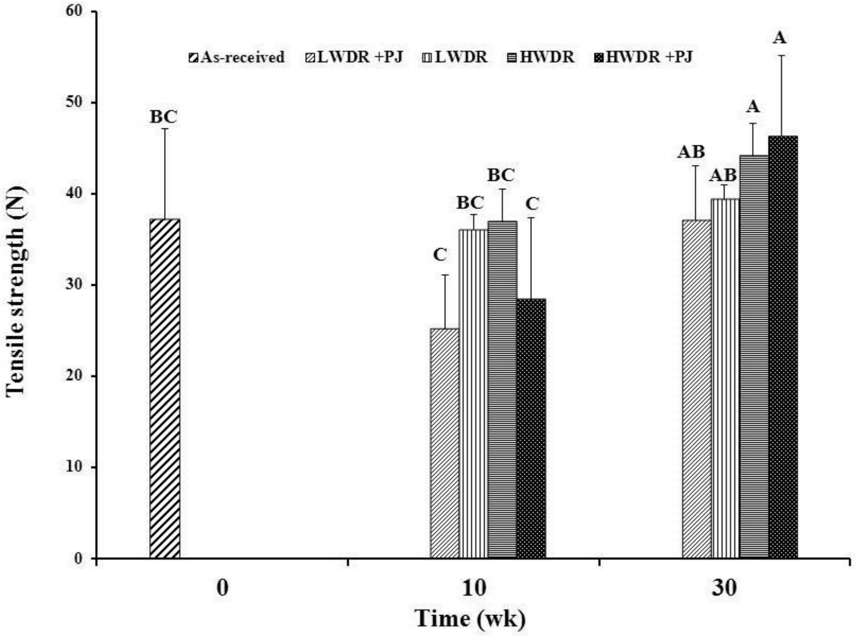


Figure 20: Comparison of tensile strength values of SB-PLA-2011 retrieved after 10 and 30 wk in Study 2. Mean values (represented by grouped bars) with no common letter groupings are statistically different (p<0.05).

3.4.4. CHANGE OF NUMBER AVERAGE MOLECULAR WEIGHT AND POLYDISPERSITY INDEX FOR NONWOVEN MULCHES

The decrease of molecular weight suggests the degradation of nonwoven PLA and PLA/PHA blends based nonwoven mulches under high moisture conditions (Table 7). Soil amendments decreased the M_n of all the mulches significantly ($p<0.001$) after 10 and 30 wk. As observed in Table 7, SB-PLA-2011 buried for 30 wk underwent the greatest decrease, 9%, for the LWDR+PJ treatment. A much greater decrease, 26%, occurred for MB-PLA+PHA-85/25 treated with low water delivery rate. Water, at high delivery rate, decreased the M_n of MB-PLA+PHA blends, 11-13%, whereas at low delivery rate, the M_n decreased by 0.9%. The decrease of M_n for SB-PLA (9%) and MB-PLA (6.3%) mulch was greater in the presence of PJ compared to water delivery rate. There was no major change of PDI values for MB and SB-PLA mulches after 30 wk (Table 7).

Table 7: Number-average molecular weight (M_n) and polydispersity index (PDI) values of mulches in Study 2

Soil amendments	Mulch	Burial time (wk)	M_n[a] (g/mol)			PDI[d]	
			Mean[b]		SE[c]	Mean[b,e]	
Untreated	SB-PLA-2011	0	1.01 X 10^5	A	1.85 X 10^3	1.29	MNOPQ
	MB-PLA		9.95 X 10^4	AB	1.66 X 10^3	1.28	OPQRS
	MB-PLA+PHA-85/15		8.99 X 10^4	H	4.12 X 10^2	1.32	HIJ
	MB-PLA+PHA-75/25		7.58 X 10^4	LM	5.55 X 10^2	1.38	ABCD
High water delivery rate (HWDR)	SB-PLA-2011	10	1.01 X 10^5	A	1.95 X 10^3	1.27	RST
		30	1.00 X 10^5	A	1.37 X 10^3	1.30	KLM
	MB-PLA	10	9.88 X 10^4	AB	1.49 X 10^2	1.25	TU
		30	9.42 X 10^4	EFG	8.25 X 10^2	1.26	TU
	MB-PLA+PHA-85/15	10	8.65 X 10^4	I	6.41 X 10^2	1.30	MNO
		30	7.92 X 10^4	K	5.88 X 10^2	1.30	MN
	MB-PLA+PHA-75/25	10	7.25 X 10^4	N	5.01 X 10^2	1.35	FG
		30	6.78 X 10^4	OPQ	8.72 X 10^2	1.36	EF

[a] Number-average molecular weight based on polystyrene standards. Means with no common letters are statistically different ($p<0.05$) ; [b] Means compared using Fisher's Least significant difference (LSD) in SAS 9.3 (2013) ;[c] Standard error; [d] polydispersity index ; [e] Standard error values <0.01

Table 7 continued: Number-average molecular weight (M_n) and polydispersity index (PDI) values of mulches in Study 2

Soil amendments	Mulch	Burial time (wk)	M_n [a] (g/mol)			PDI[d]	
			Mean[b]		SE[c]	Mean[b,e]	
HWDR + PJ	SB-PLA-2011	10	9.55 X10^{4}	CDEF	4.79 X 10^{2}	1.28	PQRS
		30	9.44 X10^{4}	EFG	1.05 X 10^{3}	1.27	QRS
	MB-PLA	10	9.64 X 10^{4}	BCDE	1.45 X 10^{3}	1.26	RSTU
		30	9.48 X 10^{4}	EFG	6.02 X 10^{2}	1.25	U
	MB-PLA+ PHA-85/15	10	7.62 X 10^{4}	L	1.04 X 10^{3}	1.33	HI
		30	7.92 X 10^{4}	K	2.85 X 10^{2}	1.31	IJK
	MB-PLA+PHA-75/25	10	6.72 X 10^{4}	OPQ	8.50 X 10^{2}	1.40	A
		30	6.61 X 10^{4}	PQ	1.04 X 10^{2}	1.38	BCD
Low water delivery rate (LWDR)	SB-PLA-2011	10	9.80 X 10^{4}	ABC	1.65 X 10^{3}	1.29	MNO
		30	9.75 X 10^{4}	BCD	880 X 10^{2}	1.30	MNO
	MB-PLA	10	9.67 X 10^{4}	BCDE	1.17 X 10^{3}	1.29	MNOP
		30	9.49 X 10^{4}	DEFG	8.55 X 10^{2}	1.28	PQR
	MB-PLA+ PHA-85/15	10	8.12 X 10^{4}	JK	1.15 X 10^{3}	1.33	GH
		30	6.60 X 10^{4}	Q	8.69 X 10^{2}	1.38	ABC
	MB-PLA+PHA-75/25	10	6.95 X 10^{4}	O	3.59 X 10^{2}	1.39	AB
		30	7.51 X 10^{4}	LM	3.81 X 10^{2}	1.37	DE
LWDR +PJ	SB-PLA-2011	10	1.00 X 10^{5}	A	8.80 X 10^{2}	1.28	PQR
		30	9.26 X 10^{4}	GH	1.22 X 10^{3}	1.29	NOPQ
	MB-PLA	10	9.83 X 10^{4}	AB	4.67 X 10^{2}	1.27	RST
		30	9.32 X 10^{4}	FG	6.83 X 10^{2}	1.26	STU
	MB-PLA+ PHA-85/15	10	8.33 X 10^{4}	J	7.39 X 10^{2}	1.31	JKL
		30	7.92 X 10^{4}	K	7.67 X 10^{2}	1.30	LMN
	MB-PLA+PHA-75/25	10	7.31 X 10^{4}	MN	5.73 X 10^{2}	1.36	EF
		30	6.91 X 10^{4}	OP	9.21 X 10^{2}	1.37	CDE

[a] Number-average molecular weight based on polystyrene standards. Means with no common letters are statistically different ($p<0.05$) ;[b] Means compared using Fisher's Least significant difference (LSD) in SAS 9.3 (2013) ; [c] Standard error; [d] polydispersity index; [e] standard error values <0.01

3.4.5. MORPHOLOGICAL CHANGE OF NONWOVEN MULCHES

In general, the decrease of values for thermal properties mirrored the decrease of M_n that occurred versus soil burial time and soil amendment. Table 8 compares the thermal properties between the "as-received" and one of the replicates of mulches for the soil treatment that yielded the greatest decrease of M_n during 30 wk of soil burial (as per Table 7). The "as-received" nonwoven, prepared from the same PLA feedstock, possessed similar T_g, T_m, and T_c values, as expected. There was a notable decrease of the T_g value for MB-PLA+PHA-85/15 due to biodegradation. The decrease of ΔH_m for the PHA and PLA components of both MB blends suggest the strong likelihood of depolymerization for both biopolymers when buried in soil. The inclusion of PHA to PLA-based MB nonwoven decreased the crystallinity; for example, ΔH_c for "as-received" MB-PLA+PHA-75/25 blends vis-à-vis MB-PLA was less (Table 7). T_g and ΔH_c of PHA component of MB-PLA+PHA blends were not determined in the DSC analysis due to thermal degradation of PHA during the first cycle, leading to the absence of crystallization peak for PHA in second cycle. The percentage of crystallinity (X_c) for PLA component of mulches decreased due to the biodegradation of amorphous content of the PLA.

Table 8: DSC results of the mulches before and after 30 wk burial in soil (Study 2)

Treatment[f]	Mulch	T_m (°C)[a]	H_m[b] (J/g)	T_g (°C)[c]	T_c (°C)[d]	H_C[e] (J/g)	X_c[h] (%)
As-received	MB-PLA+PHA-75/25 (PLA)	166.6	38.5	64.7	81.9	16.4	23.6
	MB-PLA+PHA-75/25 (PHA)	139.5	0.9	ND	ND	ND	ND
HWDR + PJ	MB-PLA+PHA-75/25 (PLA)	166.4	24	65.7	85.3	1.5	24.0
	MB-PLA+PHA-75/25 (PHA)	144.5	0.2	ND[g]	ND	ND	ND
As-received	MB-PLA+PHA-85/15 (PLA)	166.1	43.3	65.6	86.5	15	30.2
	MB-PLA+PHA-85/15 (PHA)	138.6	0.9	ND	ND	ND	ND
LWDR	MB-PLA+PHA-85/15 (PLA)	160.8	26.2	62.2	80.4	1.7	26.2
	MB-PLA+PHA-85/15 (PHA)	145	0.1	ND	ND	ND	ND
As-received	MB-PLA	167.8	52	61.5	101.5	28.5	25.1
LWDR+PJ		167.3	40.2	61.8	101.8	10.1	32.2
As-received	SB-PLA-2011-Black	164.2	53.6	61.7	96.8	21	34.8
LWDR+PJ		163.7	49	61.6	97.7	18.1	33.0

[a] Melting temperature of first heating cycle; [b] Enthalpy of fusion of first heating cycle; [c] Glass-transition temperature from second-heating cycle; [d] Crystallization temperature of second heating cycle; [e] Enthalpy of crystallization of PLA in second heating cycle; [f] For a given mulch, PJ and water delivery rate which led to the greatest decrease of number-average molecular weight in each treatment, as per Table 7, are analyzed and compared with "as-received" mulches; [g]ND-Not determined; [h] Percentage of crystallinity of PLA component of nonwoven mulches from Eqn.3

3.4.6. FTIR-ATR SPECTROSCOPY ANALYSIS OF CHEMICAL STRUCTURE FOR NONWOVEN MULCHES

The breakage or formation of chemical bonds, particularly depolymerization due to hydrolysis, was determined using FTIR-ATR spectroscopy. The most prominent regions of the peak bands observed in this soil burial study were 1759 cm^{-1}corresponding to carbonyl stretching and 3506 cm^{-1} corresponding to –OH stretching.

Figs 21 and 22 indicated major changes in PLA and PHA structure of MB-PLA+PHA-75/25 and SB-PLA-2011.The decrease of carbonyl stretching at 1759 cm^{-1} and increase of OH stretching at 3506 cm^{-1} of MB-PLA+PHA-75/25 indicated the hydrolysis is the major mechanism for depolymerization. The decrease of M_n (Table 8) correlated with increasing hydroxyl-stretching vibration and decreasing carbonyl stretching (data not shown). Other spectral changes observed for SB-PLA-2011 were the greatest decrease of intensity at 1460 cm^{-1} (–CH_3 bending), and 1382 and 1360 cm^{-1} corresponding to –CH—asymmetric and symmetric deformation for LWDR+PJ amendment (figure not shown). In a similar vein, MB-PLA+PHA-75/25 displayed a greatest decrease at 1460, 1360, and 1382 cm^{-1}for HWDR amendment compared to the "as-received" (figure not shown).

In Chapter 8, FTIR-ATR analysis was conducted for the mulches that underwent simulated weathering. There were new spectral band at positions 1585 cm^{-1} and 1718 cm^{-1} that corresponded to formation of C=C end groups and carboxylic acids, respectively. The Norrish Type II reaction mechanism corresponds to those spectral changes where UV light cleaved the ester bonds of PLA (Section 8.4.6). However, no peak at position 1585cm^{-1} was observed in the soil burial studies indicating that no photodegradation occurred because ultraviolet light could not penetrate into the top layer of the soil.

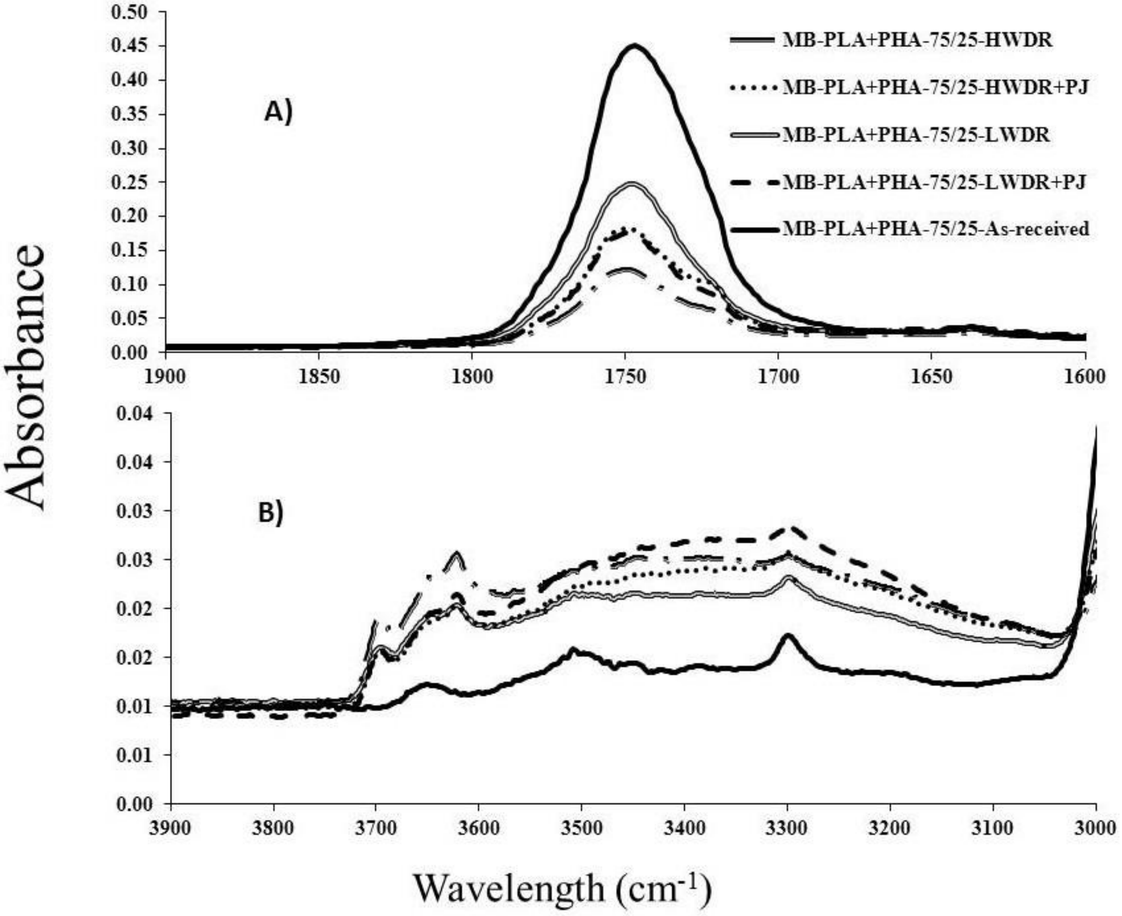


Figure 21:FTIR /ATR spectrum of mulch MB-PLA+PHA-75/25 of Study 2; A) Comparison of C=O stretching of mulch during 0 and 30 wk for all the treatments at 1759 cm^{-1}; B) Comparison of –OH stretching of mulch during 0 and 30 wk for all the treatments at 3506 cm^{-1}

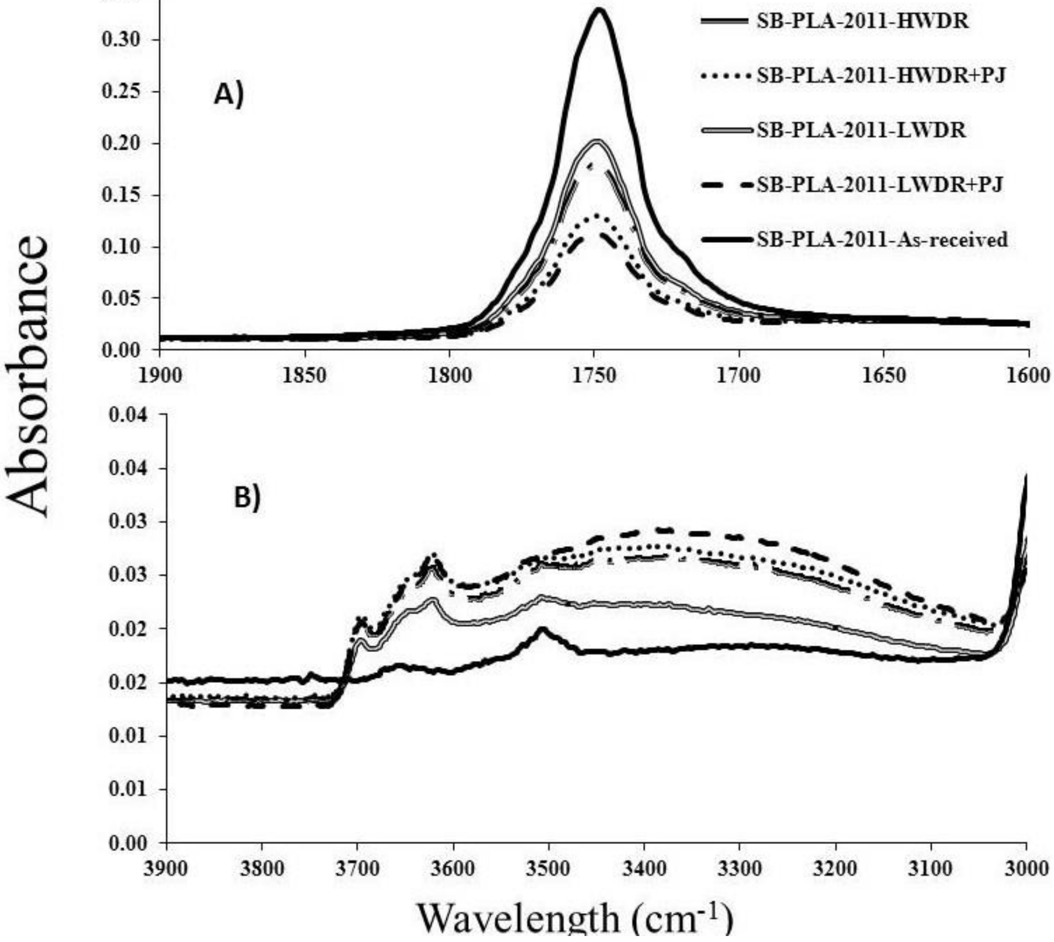


Figure 22:FTIR /ATR spectrum of mulch SB-PLA-2011 of Study 2 ;A) Comparison of C=O stretching of mulch during 0 and 30 wk for all the treatments at 1759 cm^{-1}; B) Comparison of –OH stretching of mulch during 0 and 30 wk for all the treatments at 3506 cm^{-1}

3.4.7. FIBER BREAKAGE OF NONWOVEN MULCHES

The fiber diameter of SB-PLA-2011 was greater than MB-PLA, consistent with the findings in Study 1 (Section 2.10). For MB-PLA+PHA blends, the fiber diameter was higher than that of MB-PLA due to the inclusion of PHA (Table 4). Fig.23 displays the fiber breakage of mulches retrieved from soil after 30 wk. Microfiber breakage was observed in SEM for all the four mulches, in Study 2, that underwent greatest loss of M_n due to a soil amendment. The degree of fiber breakage was highest for the MB-PLA+PHA blends as depicted in Fig.23 (C&D).

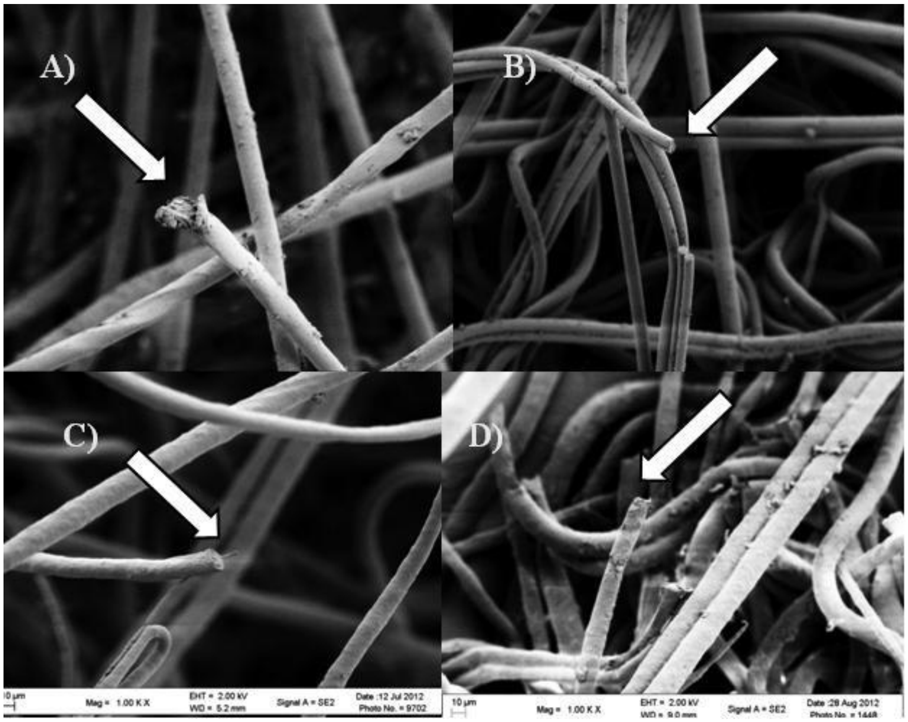


Figure 23: SEM Micrographs of mulches subjected to water delivery rate and PJ treatment that led to greatest decrease of M_n during 30 wk of Study 2 at 1000X; White arrows are pointed towards the fiber bond breakage; A) SB- PLA-2011 treated with LWDR+PJ ; B) MB -PLA treated with LWDR+PJ ; C) MB-PLA+PHA-85/15 treated with LWDR and ; D) MB- PLA+PHA-75/25 treated with HWDR + PJ.

3.5. DISCUSSION

Study 2 entailed the effect of water delivery rate and PJ, a carbon source for microorganisms of the biodegradation of SB and MB mulches prepared from PLA or PLA/PHA blends. SB nonwoven mulches underwent biodegradation to a minimal extent during the 30 wk study for all soil treatments, evidenced by negligibly small decreases of physico-chemical properties (tensile strength and M_n) after 30 wk,. However, the impact of soil amendments and nonwoven composition on biodegradation of MB mulches is more complex, and therefore requires an expanded discussion.

3.5.1. ROLE OF PINEAPPLE JUICE (PJ)

PJ is purportedly a valuable soil amendment due to of its ability to serve as a carbon source for microorganisms and its typically high content of the enzyme bromelain. However, an enzymatic assay conducted by the writer of this dissertation revealed that there was no detectable level or activity of “bromelain” in PJ—the potential limitation of Study 2. But, since PJ may serve as a carbon source for microorganisms in soil, it was therefore expected that PJ would enhance microbial assimilation of the mulches.

The significant decrease of M_n for LWDR+PJ treated MB-PLA+PHA-85/15 and MB-PLA+PHA-75/25, relative to mulches LWDR (in the absence of PJ), after 30 wk partly supports the hypothesis that PJ amendments increase the biodegradation of PLA and PLA/PHA blends nonwoven mulches.

Although there was no statistical significance between soil amendments on the decrease of tensile strength, the loss that occurred for MB-PLA+PHA-75/25 and MB-PLA was slightly reduced by the presence of PJ, possibly due to the slight decrease of soil pH promoted by PJ (Table 6). In addition, the inhibition of weed growth by PJ, observed during Study 2, may also reflect reduced microbial activity. Overall, the effect of PJ played only a minor role in the biodegradation of PLA-based nonwoven mulches.

3.5.2. ROLE OF WATER DELIVERY RATE

The water delivery rate in general affected the biodegradation of mulches to a minor extent. The application of the LWDR soil treatment led to a decrease of M_n and thermal properties for MB-PLA+PHA-85/15 to the greatest extent (~27%) after 30 wk among the mulches investigated, supported by the decrease of thermal properties. For example, T_g of MB-PLA+PHA-85/15 was decreased from 65.6 to 62^{o}C (Table 8). In contrast, the decrease of M_n for MB-PLA+PHA-75/25 due to HWDR was higher compared to LWDR (Table 7), also observed by the greater decrease of intensity of -C=O stretching at 1751 cm^{-1} analyzed by FTIR (Fig.21A), reflecting a greater extent of ester bond hydrolysis. The percent decrease of M_n for HWDR vs. LWDR was statistically insignificant for MB-PLA.

In general, the effect of water delivery rate on the biodegradation of mulches (depolymerization, loss of tensile strength and thermal properties) in Study 2 was almost not distinguishable. This trend reflects the fact that the soil moisture levels obtained via LWDR and HWDR were not statistically significant ($p>0.1$, 32±18 and 37±4% for LWDR and HWDR, respectively), and were within an optimal range, as reviewed in [114]. Therefore, both water delivery rates were equally as effective on the biodegradation of MB mulches. Future soil burial studies can be improved by employing LWDR per 24 hr—the optimal level of moisture can be achieved, as in Study 2. Additionally, the quantification of microorganisms and PLA degrading enzymatic activity of microbes can be performed.

3.5.3. INCORPORATION OF PHA IN THE MELTBLOWN MULCHES

Biodegradation of PHA under ambient soil conditions has been reported in many studies [127-132]. PHA, a biopolymer known to undergo biodegradation in many environments, has been blended with PLA to prepare a feedstock for nonwoven textile processing and investigated for biodegradation in soil in Study 2. The enhanced biodegradation of MB-PLA+PHA blends, compared to MB-PLA, supported the second hypothesis of Study 2—incorporation of PHA in PLA nonwoven mulches would increase the biodegradation

(Sections 3.4.3 and 3.4.4). To support, the incorporation of PHA decreased the crystallinity of PLA (ΔH_c for "as-received" MB-PLA+PHA blends in Table 8) and as a result, the biodegradation of PLA was increased, as evidenced by a larger decrease of tensile strength (94%) and molecular weight (30%) for MB-PLA+PHA blends. Results of Study 2 are in agreement with the findings of Weng *et al*—the biodegradation of PHA and PLA/PHA blend films evaluated under ambient soil conditions and in the presence of compost for 5 months followed the pattern: PHA-100 or [P(3HB,4HB)] > PHA+PLA-75/25 > PHA+PLA-50/50> PHA+PLA-25/75> PLA-100 [27].

3.6. CONCLUSIONS

Study 2 examines the effect soil amendments—HWDR, LWDR, HWDR+PJ, and LWDR+PJ—on the biodegradation of PLA and PLA/PHA blends nonwoven mulches in soil- and compost filled trays. SB nonwoven mulches underwent biodegradation to a minor extent for all the amendments and water delivery rates—indicated by negligibly small decrease of tensile strength after 30 wk. The depolymerization of mulches—MB to the greatest extent and SB to a less extent—was determined by gel permeation chromatography. The hydrolysis of ester bonds and formation of hydroxyl bonds of all mulches in Study 2 by soil amendments were confirmed by FTIR analysis. Among MB nonwoven mulches, MB-PLA+PHA blends underwent relatively greater biodegradation than MB-PLA for all the amendments after 30 wk—determined from depolymerization and tensile strength loss. In conclusion, low and high water delivery rates were reported to be equally effective for the biodegradation of MB-PLA+PHA blends and MB-PLA nonwoven mulches; PJ played a minor role in the biodegradation of nonwoven mulches in Study 2.

CHAPTER 4

SOIL BURIAL STUDY 3: COMPARISON OF BIODEGRADABILITY FOR PLA AND PLA/PHA BLENDS NONWOVEN MULCHES TO A COMMERCIALLY AVAILABLE STARCH-BASED BIODEGRADABLE MULCH

4.1. INTRODUCTION

The employment of starch-based film “BioTelo”—commercially manufactured by Novomont, Italy, as prepared from the proprietary blend Mater-Bi™ (Section 1.2.3)—in organic agriculture is of concern because of non-biobased additives in its composition. Kim *et al* [133], after conducting a soil burial test for a short period (55 days) to characterize the fungus degrading commercial polymers, concluded that Mater-Bi™ underwent relatively less biodegradation than PHB in a modified Sturm test. The research work described in Study 3 is the first comprehensive soil burial test comparing biodegradation of nonwoven mulches, prepared from PLA and PLA/PHA blends, to BioTelo under conditions that enhance mineralization: a high water delivery rate that leads to high moisture conditions and the inclusion of compost. It is hypothesized that BioTelo and meltblown mulches prepared from PLA/PHA blends nonwoven mulches, will undergo biodegradation at a similar rate and extent.

The biodegradation of white colored mulches is greater than black after exposure to sunlight due to photolysis [134]. It is not clear, however, if the biodegradation of (nonweathered) white and black color mulches differs during soil burial. Study 3 will address the effect of mulch color on the rate and extent of biodegradation.

4.2. OBJECTIVES

The main goal of Study 3 was to compare the biodegradation of BioTelo “biodegradable mulch film” to PLA and PLA/PHA blends nonwoven mulches under high water delivery rate conditions (1000 mL of water per 48 hr) in the presence of compost. Additionally, Study 3 also compared the biodegradable performance of white and black spunbond nonwoven mulches and neat PLA nonwoven to PLA/PHA blends nonwoven mulches. Mulches were retrieved and analyzed for the loss of tensile strength, number average molecular weight and thermal properties.

4.3. EXPERIMENTAL

4.3.1. MATERIALS

In addition to nonwoven used in Study 2 (Table 4), mulches described in Table 9 were employed for Study 3. Black Kow® Compost was purchased from Oxford, FL, USA.

4.3.2. EXPERIMENTAL DESIGN

A completely randomized design was employed as the statistical experimental design. There were seven mulches in this study: three mulches (SB-PLA-2010, SB-PLA+PHA-80/20, and BioTelo) described in Table 9 and four (MB-PLA, MB-PLA+PHA-85/15, MB-PLA+PHA-75/25, and SB-PLA-2011) described in Table 4. The experimental design included mulches with two replicates and two retrieval times (10 & 30 wk). Hence, the total number of experimental trays was 28 (7 * 2 * 2). Dewey silt loam soil, collected from USDA certified organic farm, was mixed with compost and used in this experiment. The soil moisture content, determined using Waterscout SM 100 sensors (Spectrum Technologies, Plainfield, IL, USA), was measured to be 24.14± 6.17%. Soil and air temperature, determined from sensors inserted 2 cm beneath the soil, were 15.6 ± 5.6^{o}C and 23.9 ± 3.4^{o}C, respectively. All units received a high (tap) water delivery rate (1000 mL per 48 hr)—trickled by a water can. This soil burial study, conducted in Greenhouse 16 on the UTIA campus, was started on January 26, 2012 and ended on August 23, 2012. Procedures for mulch burial, retrieval and cleaning were explained in detail in Section 3.3.3.

Table 9: Inherent properties of mulches used in Study 3

Mulch[a]	Feedstock[b]	Color	Weight[c] (g/m^2)	Fiber diameter[d] (µm)	Thickness[d] (µm)	M_n[e] (kDa)	Tensile strength (N)
SB-PLA-2010[f]	Ingeo® 6202D	White[j]	88.4 ± 2.6	14.9 ± 0.3	687 ± 32	101±1.9	56.21±2.11
SB-PLA+PHA-80/20[g]	Ingeo® 6251D (PLA) + 1-2% Carbon black + GreenBio	Black	80.7 ± 2.3	18.2±0.6	483 ± 19	91.3±1.4	43.35±2.00
BioTelo[h]	Mater-Bi™ based film (Dubois Innovation, Ontario, Canada)	Black	17.9±1.1	NA[i]	25±3	62.3±0.2	5.44±1.7

[a] SB and PHA refer to meltblown,spunbond and polyhydroxy alkanoate, respectively with weight percent of PLA and PHA given in mulch name.; [b] Ingeo® are PLA products obtained from NatureWorks, Blair, NE USA (melt indices for 6252D and 6202D are 70-85 g per 10 min and 15-30 g per 10 min, respectively. Ingeo® 6252D and 6251D are identical, except for the inclusion of a biodegradable pellet lubricant for the former), PHA obtained from GreenBio (Tianjin, China); [c] Uncertainty values reflect standard deviation ; [d] Uncertainty values reflect standard error; [e] Number-averaged molecular weight of PLA component based on polystyrene standards; [f] prepared in 2010; [g] prepared in 2012; [h] Purchased in 2010; [i] NA-Not applicable; [j] Natural color of the nonwoven and contain no titania.

4.3.3. EXPERIMENTAL METHODS

Among the experimental methods (listed in Table 5), only tensile strength testing, gel permeation chromatography and DSC were used to characterize the biodegradability of mulches. The three testing methods were explained in Sections 3.3.4.1, 3.3.4.2, and 3.3.4.3, respectively. DSC was performed only on one of the replicates of all the nonwoven mulches (except for BioTelo) and only for mulches retrieved from soil after 30 wk. Analysis of variance (ANOVA) was conducted using mixed model analysis in SAS 2013, V9.3, SAS Institute Inc., Cary, NC, USA. Mean values were calculated and compared using Fisher's Least Significance Difference method.

4.4. RESULTS

4.4.1. CHANGE OF TENSILE STRENGTH FOR NONWOVEN MULCHES

There was a significant difference ($p<0.001$) of loss of tensile strength as function of time for MB-PLAs and BioTelo. As observed from Fig.24, the tensile strength value of all the MB nonwoven mulches employed in this study decreased by 78-80% in agreement with the previous study (Study 2 in Section 3.2). Because of extreme deterioration and fragmentation after 30 wk, retrieved MB nonwoven were not tested for tensile strength. Fig.24 displays the comparison of tensile strength value of "as-received" SB mulches to the mulches retrieved after 10 and 30 wk.SB-PLA-2011 decreased by 3% after 30 wk. The tensile strength value of SB-PLA-2010—nonwoven mulch used in soil burial study 1—decrease by 8.1 and 6.0 N after 10 and 30 wk, respectively. The loss of tensile strength values as function of time for SB-PLAs were not statistically significant ($p=0.29$). Among SB mulches, the tensile strength value of SB-PLA+PHA-80/20 underwent the greatest decrease, 12%, after 30 wk, attributable to the incorporation of PHA in the mulch.

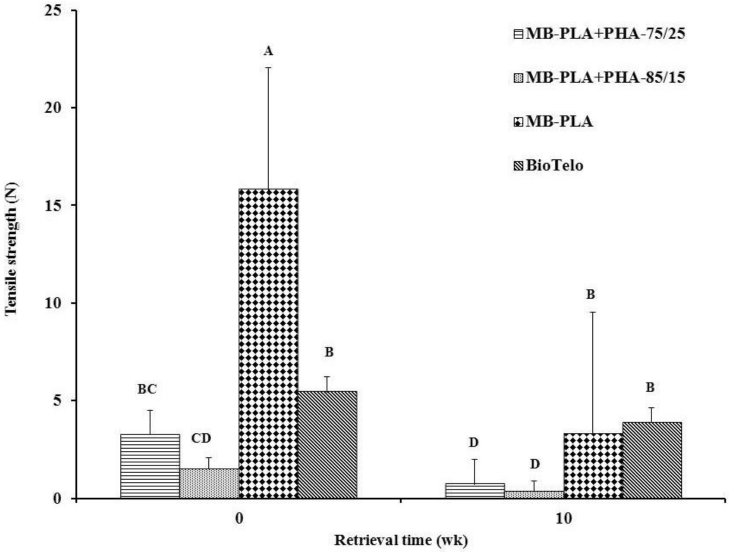


Figure 24: Comparison of tensile strength values of "as-received" (at time 0) vs. 10 wk retrieved MB and BioTelo mulches (Study 3). Mean values represented by grouped bars with no common letter groupings are statistically different (p<0.05).

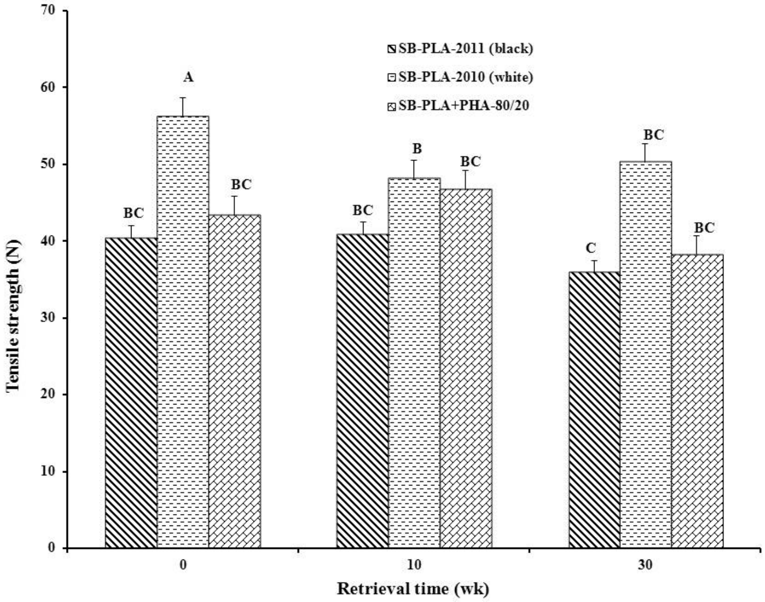


Figure 25: Comparison of tensile strength values of "as-received" (time 0) vs. 10 and 30 wk retrieved SB mulches (Study 3). Mean values represented by grouped bars with no common letter groupings are statistically different (p<0.05).

4.4.2. CHANGE OF NUMBER AVERAGE MOLECULAR WEIGHT AND POLYDISPERSITY INDEX FOR NONWOVEN MULCHES

Table 10 provides M_n and PDI values of all the mulches used in this study before and after retrieval from the burial in soil. Mixed model of ANOVA in SAS 9.3 indicated that there was a significant difference ($p<0.001$) for M_n between the mulches as a function of time. The loss of M_n for SB-PLA+PHA-80/20 mulch is the highest (12.3%) among the SB mulches used in this soil burial study. However, all the SB mulches underwent only ~11-12% loss of M_n. MB-PLA+PHA-75/25 underwent the greatest loss of M_n (30%) for the mulches studied. It was followed by MB-PLA+PHA-85/15, which underwent decrease of 17%. The marginal decrease of M_n for MB-PLA after 30 wk (93,500 g/mol) buried in soil reflected very little occurrence of depolymerization. The M_n loss for BioTelo—the only mulch film employed in Study 3—was 11.4% for its chloroform soluble components after 30 wk. For all the mulches employed in this study, there were no notable changes in the PDI values.

Table 10: Number-averaged molecular weight and polydispersity index values of mulches used in Study 3

Mulches	**Retrieval time (wk)**	**M_n (g/mol)**		**PDI[d]**
		Mean[b]	**SE[c]**	**Mean[b,e]**
MB-PLA	0	9.95 X 10^4 D	1.66 X 10^3	1.28 HI
	10	9.91 x 10^4 D	1.40 X 10^3	1.28 HI
	30	9.35 X 10^4 EF	5.52 X 10^2	1.28 HI
MB-PLA+PHA-85/15	0	8.99 X 10^4 FG	4.12 X 10^2	1.32 EFG
	10	8.18 X 10^4 H	1.32 X 10^2	1.33 E
	30	7.44 x 10^4 I	1.39 X 10^3	1.30 FGH
MB-PLA+ PHA-75/25	0	7.58 X 10^4 I	5.55 X 10^2	1.38 D
	10	7.46 X 10^4 I	7.84 X 10^2	1.32 EF
	30	5.27 X 10^4 K	9.75 X 10^2	1.47 B
SB-PLA-2011	0	1.01 X 10^5 D	1.85 X 10^3	1.29 GHI
	10	9.51 X 10^4 E	3.92 X 10^2	1.27 I
	30	9.00 X 10^4 G	2.28 X 10^2	1.28 HI
SB-PLA-2010	0	1.30 X 10^5 A	0	1.28 HI
	10	1.24 X 10^5 B	4.79 X 10^2	1.28 HI
	30	1.14 X 10^5 C	2.63 X 10^3	1.33 EF
SB-PLA+PHA-80/20	0	9.13 X 10^4 FG	1.35 X 10^3	1.31 EFGH
	10	8.99 X 10^4 G	9.07 X 10^2	1.30 FGH
	30	8.01 X 10^4 H	1.10 X10^3	1.33 E
BioTelo	0	6.23 X 10^4 J	2.32 X10^2	1.43 A
	10	6.40 X 10^4 J	9.72 X 10^2	1.43 C
	30	5.52 X 10^4 K	6.36 X 10^2	1.53 B

[a] Number-average molecular weight of chloroform soluble components based on polystyrene standards; [b] Mean values with no common letters are statistically different ($p<0.05$); [c] Standard error ; [d] polydispersity index ; [e] Standard error values <0.01

4.4.3. MORPHOLOGICAL CHANGE OF NONWOVEN MULCHES

The influence of abiotic hydrolysis and/or biodegradation on morphology of PLA and PLA+PHA blends was analyzed by DSC. Because of propriety nature of its composition, BioTelo was not analyzed via DSC. Only minor changes of T_g, T_m and T_c for all the mulches used in this study were observed (Table 11). The T_m value of MB-PLA+PHA-75/25 was reduced by the greatest degree (3.6%)—in agreement with the mulch's large reduction of M_n (Table 10). The change of melting enthalpy (ΔH_m) for the mulches also represented depolymerization. When comparing "as-received" SB and MB nonwoven, the addition of PHA for both nonwoven types reduced the degree of crystallinity; as observed from the decrease of value of ΔH_c (Table 11), the crystallinity was further reduced largely in both the mulches after buried in soil. The percentage of crystallinity of PLA (X_c) greatly decreased in most of nonwoven mulches due to hydrolysis.

Table 11: Thermal properties of mulches before and after 30 wk of Study 3

Mulch	Retrieval time	T_m[a] (°C)	ΔH_m[b] (J/g)	T_g (°C)	T_c (°C)	ΔH_c[e] (J/g)	X_c[f] (%)
MB-PLA+PHA-75/25 (PLA)	0	166.6	38.5	64.7	81.9	16.4	23.6
	30	160.6	25.2	66.1	82.9	0	26.9
MB-PLA+PHA-75/25 (PHA)	0	139.5	0.9	ND[g]	ND	ND	ND
	30	140.2	0.2	ND	ND	ND	ND
MB-PLA+PHA-85/15 (PLA)	0	166.1	43.3	65.6	86.5	15	30.2
	30	166.7	28.9	66.3	84.1	0	30.9
MB-PLA+PHA-85/15 (PHA)	0	138.6	0.9	ND	ND	ND	ND
	30	142.1	0.4	ND	ND	ND	ND
MB-PLA	0	167.8	52	61.5	101.5	28.5	25.1
	30	167.4	21.7	62.9	104.7	5.7	17.1
SB-PLA-2011	0	164.2	53.6	61.7	96.8	21	34.8
	30	163.3	26.8	62.9	98.8	13.1	14.6

[a] Melting temperature of first heating cycle ; [b] Enthalpy of fusion of the first heating cycle ; [c] Glass transition temperature of second heating cycle ; [d] Crystallization temperature of second heating cycle ; [e] Enthalpy of crystallization of PLA of second heating cycle ; [f] Percentage of crystallinity of PLA determined from Eqn.3 ; [g] ND=Not determined

Table 11 Continued: Thermal properties of mulches before and after 30 wk of Study 3

Mulch	Retrieval time (wk)	T_m[a] (°C)	ΔH_m[b] (J/g)	T_g (°C)	T_c (°C)	ΔH_c[e] (J/g)	X_c[f] (%)
SB-PLA-2010	0	163.6	40.4	62.3	113.7	28.2	13.0
	30	162.8	33.5	62.1	112.6	17.6	17.0
SB-PLA+PHA-80/20 (PLA)	0	168.0	33.1	51.9	83.1	5.9	36.3
	30	165.8	20.6	58.5	97.7	6.3	19.1
SB-PLA+PHA-80/20 (PHA)	0	135.5	0.5	ND	ND	ND	ND
	30	140.3	0.1	ND	ND	ND	ND

[a] Melting temperature from first heating cycle; [b] Enthalpy of fusion of the first heating cycle; [c] Glass transition temperature of second heating cycle; [d] Crystallization temperature from second heating cycle; [e] Enthalpy of crystallization of PLA from second heating cycle ; [f] Percentage of crystallinity of PLA; [g] ND=Not determined

4.5. DISCUSSION

4.5.1. COMPARISON OF BIODEGRADATION FOR WHITE vs. BLACK COLORED SPUNBOND NONWOVEN MULCHES

An objective of Study 3 was to test whether the white colored SB mulches will undergo biodegradation to a greater extent and rate than black colored SB mulches, as reported to occur in field studies[135, 136]. Results of Study 3 indicate that there is no statistically significant difference between degradation of white and black spunbond (SB) nonwoven mulches for their loss of tensile strength and molecular weight, and changes in thermal properties.

Both black and white-colored SB nonwoven mulches are recommended for use in long-term agricultural applications such as row covers and landscape fabrics. White colored mulches would reduce the soil temperature during summer due to reflectivity of sunlight and black colored SB mulches would increase soil temperature due to absorption of sunlight and hence is recommended during winter [137]. In addition, black colored SB mulches were determined to be more effective for preventing weed growth during field studies [135, 136].

4.5.2. BIOTELO MULCH FILMS vs. NONWOVEN MULCHES

It was postulated that the MB-PLA+PHA mulches, determined to undergo the greatest extent of biodegradation among the nonwoven mulches in Study 2 (Chapter 3), undergo biodegradation to a similar rate and extent as a partially “biobased” film BioTelo. Results of Study 3 support the hypothesis—the rate and extent of biodegradation of the nonwoven mulches is greater than for BioTelo.

Possibly, abiotic weathering (e.g. sunlight) is required as a pretreatment to allow for enhanced biodegradation of BioTelo. For instance, a field study—conducted in 2010 at TN, WA, and TX for 3-4 months that employed several mulches, including BioTelo—suggested that deterioration of BioTelo was more pronounced in the region that possessed higher temperature and sunlight exposure (TX) compared to other regions (TN, WA) [135].

A concern with the use of BioTelo mulch film is “partially biobased”, containing propriety fossil-fuel derived polyesters and additives. Fossil fuel derived feedstocks possesses poor environmental sustainability, due to possible destruction of nature that may occur due to mining, and the increased production of CO_2, a greenhouse gas attributable to climate change. It is probable that based on US National Standard Organic Board (NOSB) criteria for biobased content—explained in detail in Chapter 8—BioTelo might be ruled out as agricultural plastics in US organic fields. In contrast, the MB nonwoven mulches tested in this dissertation are fully biobased, consisting of the biopolymers PLA and PHA.

4.5.3. CHANGES IN MORPHOLOGY OF PLA

DSC was used to monitor the morphological changes and percentage of crystallinity of PLA. One of the DSC derived measurements,the glass transition temperature (T_g) is related to number-average molecular weight (M_n) by the Fox-Flory equation [138]:

$$T_g = T_{g\infty} - \frac{A}{M_n} \qquad (\mathbf{4})$$

where T_g is the glass transition temperature, $T_{g\infty}$ is the T_g for very high M_n and "A" is the constant term determined empirically. According to Eqn. 2, the depolymerization of PLA decreases T_g, confirmed by many studies [139, 140]. The underlying mechanism that would lead to a decrease of T_g is hydrolysis, promoted by the adsorption of water by PLA. Interestingly, there was a slight increase of T_g (Table 11) for all the nonwoven mulches perhaps due to the restriction of motion of the rigid amorphous fraction (RAF)—the intermediate phase that forms during the transition from crystalline to amorphous phase behavior—on the segmental dynamics of semi-crystalline polymer (PLA) chains [123, 141]. In addition, van der Waals bonds between the amorphous regions prevent the entry of water and its plasticizing action on the polymer[142] . During a soil burial study carried out in Finland forest soil for 24 months, the above mentioned changes in the morphology of PLA were observed [143]. The value of T_m remained almost constant throughout the Finland forest soil study because the plasticizing effect of water did not affect the thicker crystalline, PLA rich region [123, 143]. In addition, the percent of crystallinity of PLA (X_c) increased after 30 wk burial in soil , attributable to selective degradation of amorphous part of fiber coupled with migration and biodegradation of low molecular weight PLA [143]. Thus, morphological changes in PLA nonwoven mulches—MB-PLA+PHA-75/25 and SB-PLA-2010—before and after burial in Study 2 i.e., the increase of crystallinity for the PLA component (X_c), may be analogous to the one conducted in Finland.

4.5.4. INCLUSION OF PHA IN SB AND MB NONWOVEN MULCHES

The incorporation of PHA in the SB-PLA nonwoven mulches increased the degradation—decrease of tensile strength and M_n, the latter to a small degree. All the spunbond nonwoven mulches, regardless of inclusion of PHA, require a longer burial time (> 1 year) than in Studies 2-3 for a notable changes in morphology and physico-chemical properties.

The enhanced biodegradation of MB-PLA+PHA blends, compared to MB-PLA, was also observed in Study 3—determined from tensile strength and M_n (Sections 4.4.1 and 4.4.2). To support, the incorporation of PHA decreased the crystallinity of PLA (cf. ΔH_c for "as-received" MB-PLA+PHA blends in Table 11) and as a result, the biodegradation of PLA was increased, as evidenced by a decrease of tensile strength and molecular weight.

4.6. CONCLUSIONS

Study 3 was conducted to compare the commercially available partial biobased and biodegradable mulch film "BioTelo" to PLA and PLA+PHA blends nonwoven at a high water delivery rate. In addition, SB-PLA-2010 (white) was compared to SB-PLA-2011 (black)—in order to study the effect of color of mulches on biodegradation. The tensile strength of all the MB mulches in Study 3 underwent 79-80% loss after 10 wk, in agreement with Study 2.The M_n loss of MB mulches followed the order: MB-PLA+PHA-75/25 (30%) >MB-PLA+PHA-85/15 (17%) > MB-PLA (6%). The change of thermal properties (T_g, T_m, ΔH_m, and ΔH_c) reflected depolymerization of MB mulches and support the loss of crystallinity after 30 wk. The loss of tensile strength after 10 wk for BioTelo was only 27%. The M_n of BioTelo was decreased by only 11% after 30 wk. When comparing with BioTelo, MB-PLA+PHA blends underwent greater biodegradation. The biodegradation of SB-PLAs were compared for the effect of color and PHA inclusion. The loss of tensile strength of all SB-PLA-white and black was negligibly small. However, SB-PLA+PHA-80/20 underwent 11% loss of tensile strength after 30 wk, attributable to the incorporation of PHA in the nonwoven material. All of the SB-PLA mulches investigated underwent a 11% decrease of M_n. DSC results of the SB-PLA+PHA-80/20 confirmed the depolymerization of PHA. Therefore, there was no significant difference in the biodegradation of SB mulches after 30 wk. In conclusion, the results suggested that biodegradation of MB nonwoven mulches was greater than BioTelo. The biodegradation of SB nonwoven mulches were almost equivalent to BioTelo. The biodegradation of MB and SB nonwoven mulches increased to a greater and lesser extent, respectively by the inclusion of PHA.

CHAPTER 5

SOIL BURIAL STUDY 4: COMPARISION OF BIODEGRADATION TO ABIOTIC HYDROLYSIS OF NONWOVEN MULCHES

5.1. INTRODUCTION

The biodegradation of PLA under composting conditions, i.e., ≥ 58^{o}C, has been reported by many studies [109, 144], including Chapter 8 of this dissertation. The biodegradation mechanism at composting condition often involves abiotic hydrolysis reducing the molecular weight of PLA, followed by microbial assimilation using monomer, lactic acid, as a carbon energy source [145-147] . However, the role of abiotic depolymerization and microorganisms on the biodegradation of PLA is not fully understood, particularly under ambient soil conditions. In order to investigate the mechanism involved in the biodegradation of polymers, Study 4 was conducted under sterile and nonsterile conditions of soil.

5.2. OBJECTIVE

The objective of this soil burial study was to differentiate between microbial degradation and abiotic hydrolysis, as the underlying cause of the physico-chemical changes observed for the mulches in Studies 2-3. The retrieved nonwoven mulches were analyzed for a decrease of tensile strength, number average molecular weight and thermal properties.

5.3. EXPERIMENTAL

5.3.1. MATERIALS

MB-PLA+PHA-75/25 was the only nonwoven mulch used in this study. Its description was given in Table 4. Black Kow® Compost was purchased from Oxford, FL, USA.

5.3.2. EXPERIMENTAL DESIGN

A completely randomized statistical design was used in this study. The experiment was started at November 15, 2012 and ended on January 26, 2013.The duration of this experiment was relatively short (10 wk) due to difficulty in maintaining sterile conditions for a long period. In this study, the aluminum trays of same dimensions (52 cm L x 25 cm W x 6 cm D) with no drainage holes replaced plastic trays. Nonwoven mulch (MB-PLA+PHA-75/25), three replicates, and two soil treatments (sterilized and unsterilized) were employed in this study. Hence, the total number of trays was six (1 * 3 * 2). Prior to the experiment, three aluminum trays filled with soil (Dewey silt loam collected from USDA certified organic farm) and compost (Black kow), were sterilized by autoclaving at 250°C for an hour that killed most of the microorganisms' native to soil (Table 12). The sterilization process was repeated for 3x times. All of the trays were covered with aluminum foil on top to avoid the entry of air-borne microorganisms. Deionized (and sterilized) water and tap water were provided (1000 mL of water trickled using water can) on three alternative days for the sterilized and nonsterilized soil, respectively.

5.3.3. EXPERIMENTAL METHODS

The experimental methods used to characterize the biodegradation of mulches after 10 wk are:

1. GPC—This method is described in Section 3.3.4.2
2. DSC—This method is described in Section 3.3.4.3
3. Tensile strength testing—An Instron model 5567 Tensile tester (Norwood, MA, USA), located in Center for renewable Carbon at UTIA campus, was employed for this study. The procedure for tensile testing was same as employed for the previous studies (Section 3.3.4.1).
4. In addition, microbial plate counts to quantify actinomycetes and bacteria were performed before and after the experiment. The procedure of soil microbial analysis is given in the following section.
5. Analysis of variance was performed using mixed model in SAS 9.3 and least square means compared with Fisher's least significance difference.

5.3.3.1. SOIL MICROBIAL QUANTIFICATION

Soils from the three replicates of sterile and nonsterile experimental trays were collected at 0 and 10 wks. The soil samples of sterilized and nonsterilized experimental trays were serially diluted for plating to estimate bacteria and actinomycetes. Serial dilution was performed and the spread plate method was used for plating 3 replicates of dilution of 10^{-1}, 10^{-2}, and 10^{-3}, whereas dilution of 10^{-4} and 10^{-5} were used for nonsterilized soil

[148]. The peptone yeast agar media for plating bacteria consisted of: peptone, 2.5 g; yeast extract, 1.5 g; agar, 7.5 g; 1M $CaCl_2$, 5 mL. The above-mentioned materials were dissolved in 500 mL of distilled water. The glycerol casein agar media for plating actinomycetes consisted of: glycerol,4.25 mL; casein,0.25 g; KNO_3, 1 g; NaCl, 1 g; $MgSO_4.7H_2O$, 0.025 g; $CaCO_3$,0.01 g.; KH_2PO_4, 1 g; $NaHCO_3$, 0.2 g; $FeSO_4 .7H_2O$, 0.005 g; cyclohexamide, 25 mg; and agar, 9 g and dissolved in 500 mL of distilled water[148]. Ms. Rachel N. Dunlap, an undergraduate research associate, performed the quantification of soil microbes.

5.4. RESULTS

5.4.1. QUANTIFICATION OF MICROBES

The biodegradability of MB-PLA+PHA-75/25 mulch was compared in sterilized and nonsterilized compost-filled soil placed in the aluminum trays. The sterilization procedure reduced the abundance of cultivatable microorganisms, evident from the plating counts for the soil samples (Table 12). The number of microorganisms in nonsterilized soil decreased after 10 wk. Water evaporated away eventually and mulch was retrieved after 10 wk. There was a statistically significant difference of microorganisms ($p<0.001$) between sterilized and nonsterilized soil. The bacterial population increased in sterilized trays after 10 wk; however, the number of bacteria and actinomycetes in sterilized soil was less than nonsterilized soil.

Table 12: Microbial population at the beginning and end of Study 4

Treatment	Time	Actinomycetes[a]	Bacteria[a]
Sterilized soil	0	0±0.1 **C**	0±0.1 **D**
	10	$2.33 \times 10^3 \pm 8.81 \times 10^2$ **C**	$1.20 \times 10^5 \pm 2.31 \times 10^4$ **C**
Nonsterilized soil	0	$3.63 \times 10^5 \pm 6.23 \times 10^4$ **A**	TMTC[b] **A**
	10	$2.07 \times 10^5 \pm 2.67 \times 10^4$ **B**	$3.53 \times 10^5 \pm 1.12 \times 10^5$ **B**

[a] Expressed in Colony Forming Units per gram of soil with standard error. Means compared using Fisher's Least significance difference in SAS 9.3(2013).Mean values with no common letter groupings are statistically significant ($p<0.05$) ; [b] TMTC=Too many to count.

5.4.2. EFFECT OF STERILIZATION ON CHANGE OF TENSILE STRENGTH FOR MB-PLA+PHA-75/25

There was a significant difference between the tensile strength values of mulches buried in sterilized and nonsterilized soil ($p=0.006$). Moreover, the MB-PLA+PHA-75/25 mulch underwent a much greater tensile strength loss in nonsterilized soil (42%) than in the sterilized soil (3%) (Fig.26).

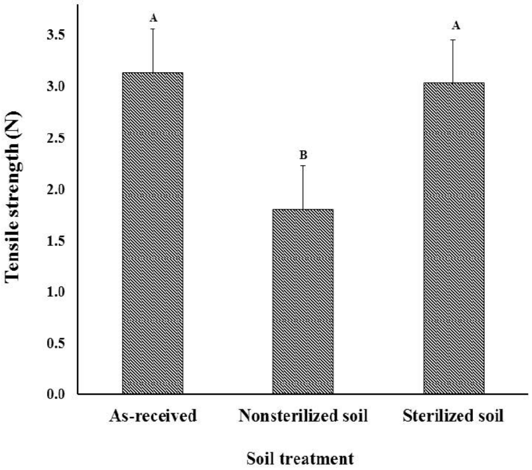


Figure 26: Tensile strength comparison of "as-received" mulch vs. mulch in sterilized and nonsterilized soil. Mean values with no common letter groupings are statistically different ($p<0.05$).

5.4.3. EFFECT OF STERILIZATION ON CHANGE OF NUMBER AVERAGE MOLECULAR WEIGHT AND POLYDISPERSITY INDEX FOR MB-PLA+PHA-75/25

The M_n value of mulch in nonsterilized soil reduced by 14%, whereas M_n for mulch retrieved from sterilized soil was reduced by 9%. Therefore, there was a slight but a significant difference between M_n loss of mulches in sterilized and nonsterilized soil ($p=0.0135$), suggesting that depolymerization was enhanced by microbial assimilation. The variation of PDI values for mulches in nonsterilized and sterilized soil relative to "as-received" mulches was negligibly small (Table 13).

Table 13: Comparison of number-average molecular weight and polydispersity index values of "as-received" mulch versus mulch in sterilized and nonsterilized soil (Study 4)

Soil Treatment	**M_n [a] (kDa)**		**PDI[d]**
	Mean[b]	**SE[c]**	**Mean[b,e]**
As-received	75.8 **A**	0.6	1.38 **A**
Nonsterile	65 **B**	2.1	1.36 **AB**
Sterile	69.3 **AB**	0.7	1.34 **B**

[a] Number-average molecular weight based on polystyrene standards; [b] Means compared using Fisher's Least significance difference in SAS 9.3(2013). Mean values with no common letters are statistically different ($p<0.05$); [c] Standard error ;[d] polydispersity index; [e] standard error values < 0.01

5.4.4. MORPHOLOGICAL CHANGE OF NONWOVEN MULCHES

The values of T_g increased for the mulches in sterilized and nonsterilized soils. When comparing ΔH_m values of the PHA and PLA, the depolymerization of PHA was more pronounced than PLA (Table 14). The melting and crystallization enthalpies, H_m and H_c, respectively, decreased for PLA and PHA, and PLA, respectively, reflecting morphological changes. Collectively, the changes of these properties for PLA reflect an increase of its percent crystallinity, X_c, suggesting that PLA selectively undergoes depolymerization in amorphous regions, thereby increasing the overall crystallinity, as discussed in Chapter 4. However, the changes of thermal properties and X_c between soil treatments was negligible.

Table 14: Comparison of DSC results of "as-received" mulch to mulch retrieved after 10 wk from sterilized and nonsterilized soil in Study 4

Soil Treatment	T_m[a] (^oC)	ΔH_m[b] (J/g)	T_g[c] (^oC)	T_c[d] (^oC)	ΔH_C[e] (J/g)	X_c[g] (%)
As-received (PLA)	166.6	38.5	64.7	81.9	16.4	23.6
As-received (PHA)	139.5	0.9	ND[f]	ND	ND	ND
Nonsterile (PLA)	168.1	33.9	66.2	83.1	2.7	33.3
Nonsterile (PHA)	142.8	0.5	ND	ND	ND	ND
Sterile (PLA)	167	33.9	65.8	86.1	3.5	32.5
Sterile (PHA)	144.2	0.3	ND	ND	ND	ND

[a] Melting temperature of first heating cycle ; [b] Enthalpy of fusion or melting enthalpy of first heating cycle ;[c] Glass-transition temperature of second heating cycle; [d] Crystallization temperature of second heating cycle; [e] Enthalpy of crystallization of PLA of second heating cycle ; [f] Not determined ; [g] percentage of crystallinity of PLA determined from Eqn.3

5.5. DISCUSSION

The purpose of this study is to distinguish the biodegradation from abiotic hydrolysis. Results of Study 4 confirm that the role of microorganisms in the biodegradation of MB-PLA+PHA-75/25 rather than abiotic factors such as moisture.

5.5.1. EFFECT OF SOIL STERILIZATION AND EXPERIMENTAL CONDITIONS ONTENSILE STRENGTH AND NUMBER AVERAGE MOLECULAR WEIGHT LOSS

Certainly, the loss of tensile strength for nonwoven mulches in unsterilized soil can be attributed to biodegradation, due to the absence of tensile strength loss occurring in the sterilized soil. These results replicate the findings of Karamanlioglu *et al* [149], where microorganisms directly assimilate PLA rather than a two-step process that involves the chemical (abiotic) hydrolysis of PLA, followed by microbial degradation. Several studies reported the isolation of actinomycetes in PLA degradation [150-154]. The microbial degradation of textiles and fibers, determined from the decrease of physical and chemical properties, in the presence of optimum level of moisture has been reviewed in [155] . The classification of actinomycetes and identification of their PLA degrading enzymatic activity are yet to be explored. The decrease of M_n for MB-PLA+PHA-75/25 mulch buried in sterilized soil, 9%, being less than the decrease that occurred in nonsterilized soil, 14%, also reflects the role of microbial activity for depolymerization. The relatively short duration of Study 4, 10 wk, did not allow for a major change in thermal properties or molecular weight to be observed.

5.5.2. EFFECT OF STERILIZATION AND EXPERIMENTAL CONDITIONS ON MICROBIAL ACTIVITY

Although the experimental protocol was designed to prevent microorganisms from residing in sterilized soil, and to enhance microorganism growth and activity in unsterilized soil through the addition of compost and employment of high soil moisture, the results of Study 4 demonstrate that these goals were not completely achieved. After 10 wk of soil burial, the number of microorganisms in nonsterilized trays decreased (Table 12). Perhaps the high water delivery rate employed in Study 4 might have changed the c biodegradation pathway from aerobic to anaerobic since water may have been above the saturation level. Perhaps the sterilized conditions—or sterilization procedure that rendered microorganisms activity initially—is not effective for 10 wk time, supported by the detection of microorganisms (bacteria and *actinomyetes*) in the sterilized soil after 10 wk, thereby explaining the relatively smaller reduction of tensile strength, M_n, and X_c for MB-PLA+PHA-75/25 mulch buried in sterilized soil.

5.6. CONCLUSIONS

In order to understand and differentiate the abiotic hydrolysis from microbial degradation, Study 4 was conducted, in which the changes in physic-chemical properties of mulch were compared in sterilized versus nonsterilized soil for 10 wk duration. The loss of tensile strength and M_n for MB-PLA+PHA-75/25 occurred more strongly in unsterilized soil compared to sterilized soil, suggesting the changes are primarily due to microbial activity rather than abiotic events. In conclusion, meltblown mulches prepared from PLA/PHA blends are assimilated by microorganisms under ambient soil conditions, and degradation is the largely due to action of microorganisms. These results suggest that the observed changes of physico-chemical properties for the MB mulches in soil burial Studies 2 and 3 are mainly attributable to microbial biodegradation as well.

CHAPTER 6

SOIL BURIAL STUDY 5: EFFECT OF SOIL TEMPERATURE ON BIODEGRADATION OF PLA BASED MELTBLOWN NONWOVEN MULCHES

6.1. INTRODUCTION

Studies 2-4 demonstrated that water delivery rates which yield optimal moisture condition (32-37%) [114], led to a partial mineralization of PLA based nonwoven mulches. However, the effect of another important abiotic factor, soil temperature, on the biodegradation of MB mulches was not investigated in Studies 2-4. In addition to moisture and pH, temperature, is the one of the most important soil-related environmental factors that affect the soil microbial growth and activity [156]. Thermophiles are predominantly found in decaying either manure or compost piles due to high temperature (50-60^{o}C). Mesophilic conditions (e.g., 20-37^{o}C), prevailing throughout most of the continental USA, are the most conducive for high microbial growth and activity. The number and activity of microorganisms decrease during winter or at low temperature (e.g. 10-15^{o}C) [116].Thus, the effect of low temperature on physico-chemical properties of nonwoven mulches pertains to low microbial activity and vice versa, in Study 5.Elevated temperature and high moisture facilitate the biodegradation of PLA, as reported in [109, 147, 157].

The influence of temperature on reaction rate is described by the Arrhenius equation [158]:

$$k = A\, e^{\frac{-E_a}{RT}} \qquad \textbf{(5)}$$

where k is degradation rate constant and A is the pre-exponential constant, representing molecular collision frequency and the unit of A depends on reaction order. For instance, if the reaction is first-order, then the units for A are s^{-1} or min^{-1} or day^{-1}. E_a (J mol^{-1}) – refers to the activation energy is the minimum free energy required for the reaction to start spontaneously. According to transition-state theory, the activation energy is the difference in energy between atoms or molecules in an activated or transition-state configuration and the corresponding atoms and molecules in their initial configuration [159]. R is gas constant (8.304 J mol^{-1}K^{-1}) and T is the absolute temperature (K). Eqn.5 defines the dependence of rate constant on temperature. Analogous to Eqn.5, is the temperature coefficient equation, employed to describe the effect of temperature on biological reaction processes [160]:

$$Q_{10} = \frac{R_1}{R_2}^{\frac{10\,K}{T_2 - T_1}} \qquad \textbf{(6)}$$

where Q_{10} is temperature coefficient, R_1 and R_2 are the reaction rates at temperatures T_1 and T_2, respectively. Q_{10} typically varies between 2 and 3, equivalent to increasing the reaction rate two-to-three-fold for an increase of 10 K. E_a for soil biodegradation of PLA is 30 (kJ/mol)[161]. If the soil temperature is increased by 10K i.e., from 298.15 K to 308.15 K, then the rate constant of biodegradation of PLA at 308.15K, according to Eqns.4 and 5, is increased 1.5-fold. Thus, the biodegradation rate of PLA based mulches is increased substantially by a minor increase of soil temperature.

An effort was made to simulate the elevated soil temperature in order to understand the biodegradation of MB mulches in a warm environment (summer). In addition, the soil temperature during moderate weather (autumn and spring) was also simulated by employing laboratory ambient conditions, which yield lower air temperatures than greenhouse conditions. Thus, Study 5 examines the importance of soil temperature on the biodegradation of MB mulches.

6.2.OBJECTIVE

Study 5 was conducted to discern the biodegradation behavior of MB-PLA and MB-PLA+PHA blends between the warmer (summer-like) and cooler (autumn and spring-like) environments. The objective of Study 5 is to understand the influence of soil temperature on the biodegradation of MB-PLA and MB-PLA+PHA-75/25 nonwoven mulches buried in soil-filled compost trays for 30 wk period.

6.3. EXPERIMENTAL

6.3.1. MATERIALS

Two mulches were used in this study:

1. MB-PLA
2. MB-PLA+PHA-75/25

The inherent properties and feedstock of the two nonwoven mulches were provided in Table 4.

6.3.2. EXPERIMENTAL DESIGN

A completely randomized statistical experimental design was employed for two mulches with three replicates and three retrieval times (10, 20, & 30 wk) at three different soil temperatures (15, 20 and 23°C). Hence, the total number of experimental trays was 54 (2 * 3 * 3 * 3). Three different soil temperatures, employed in this study, were implemented as follows (Table 15): ambient soil temperature in the greenhouse environment (control), at ~3°C above ambient soil temperature, by employing a heating pad, and at <5°C compared to ambient soil temperature in the greenhouse, simulated by employing ambient conditions in the laboratory (317 Ellington Plant Sciences). Aluminum trays, similar to those employed for Study 4 (Section 5.3.2), were used in this study. Soil and air temperature were monitored and measured using Waterscout SM 100 sensors (Spectrum Technologies, Plainfield, IL, USA) inserted 2 cm beneath the soil in aluminum trays. All units received a high water delivery rate (1000 mL per 48 hr)—tap water trickled by a watering can. The 30 wk soil burial study was started on June 25, 2012 and ended on January 26, 2013. Soil moisture content, recorded by sensors, was 21.70 ± 3.23%. Procedures for mulch burial, retrieval and cleaning were explained in Section 3.3.3.

Table 15: Air and soil temperature of trays located at three different places

Location / Environment	Laboratory ambient conditions	Greenhouse ambient conditions	Greenhouse employing heating pads
Air temperature [a] (^oC)	16.81±1.84	21.76±4.70	21.83±3.97
Soil temperature [a] (^oC)	15.46±1.83 (Control-5^oC)	20.60±4.53 (Control)	23.46±2.45 (Control+3^oC)

[a] Average temperature for 30 wk of Study 5 with standard deviation

6.3.3. EXPERIMENTAL METHODS

Among the methods listed in Table 5, these methods employed for physico-chemical analysis in Study 5 consisted of the following:

I. Tensile strength testing: This method was discussed in detail in Section 3.3.4.1
II. GPC (molecular weight analysis): This method was discussed in detail in Section 3.3.4.2
III. DSC (thermal properties): Discussion for this method was provided in Section 3.3.4.3.This was performed on one of the three replicates of the 30 wk mulches located at three different locations and compared with as-received mulch.
IV. FTIR-ATR: This method, explained in Section 3.3.4.5, was employed on one of the three replicates of the mulches retrieved at 30 wk located at three different locations and compared with “as-received” mulch.

An analysis of variance (ANOVA) was conducted using mixed model in SAS 2013, V9.3, SAS Institute Inc., Cary, NC, USA. Mean values were calculated and compared using Fisher’s Least Significance Difference method.

6.4. RESULTS

6.4.1. CHANGE OF TENSILE STRENGTH FOR MELTBLOWN MULCHES VERSUS SOIL TEMPERATURE

The effect of temperature on tensile strength loss for MB-PLA+PHA-75/25 and MB-PLA differed between the two mulches (Fig.27). An increase of soil temperature decreased the tensile strength of MB nonwoven mulches after 10 wk significantly ($p<0.01$). The loss of tensile strength value for MB-PLA+PHA-75/25, vis-à-vis "as-received", was 94% at a soil temperature of 23^{o}C. The loss of tensile strength values is attributable to the microbial degradation (Study 4, [149]). MB-PLA, intriguingly, underwent higher loss of tensile strength value (92%) at lower soil temperature (15^{o}C) compared to higher soil temperature (66% at 23^{o}C). Due to extreme fragmentation, neither MB mulch could be tested for tensile strength at 30 wk.

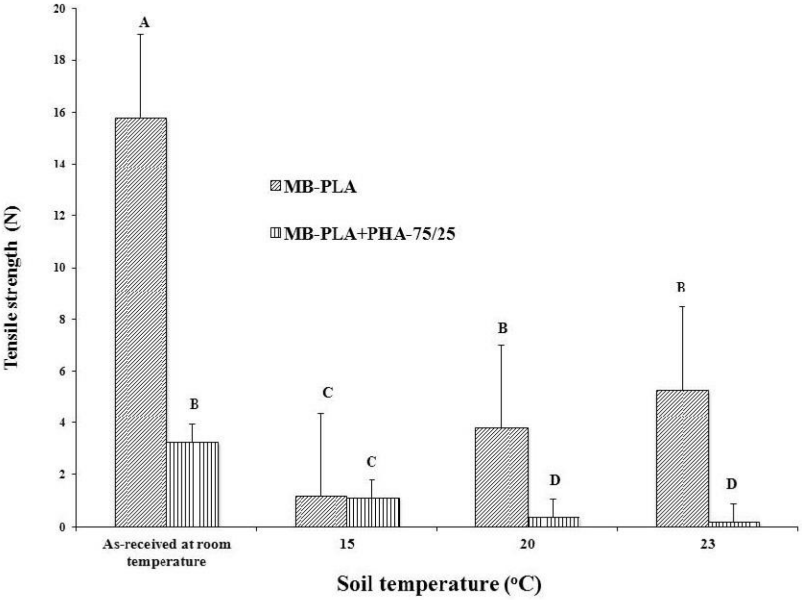


Figure 27: Comparison of tensile strength value of "as-received" to nonwoven mulches retrieved from soil at three different soil temperatures after 10 wk in Study 5. Mean values represented by bars with no common letter groupings are statistically different ($p<0.05$)

6.4.2. CHANGE OF NUMBER AVERAGE MOLECULAR WEIGHT AND POLYDISPERSITY INDEX FOR MELTBLOWN MULCHES VERSUS SOIL TEMPERATURE

Table 16 provides M_n and PDI values for the MB nonwoven mulches at three different soil temperatures and three retrieval times. The M_n of nonwoven mulches decreased significantly ($p=0.0487$) after 10, 20, and 30 wk at the three different soil temperatures. At the higher soil temperature (23^{o}C), for each of the retrieval times, the MB-PLA underwent the greatest percent decrease of M_n. After 30 wk and a soil temperature of 23^{o}C, the M_n value of MB-PLA decreased by 28%, whereas MB-PLA+PHA-75/25 decreased by 14%. The increase of temperature also increased the loss of M_n for MB mulches. However, the loss of M_n at 23^{o}C for MB-PLA+PHA-75/25 was almost equivalent to 20^{o}C—indicated by same letter groupings (Table 16). A larger decrease of M_n for MB-PLA+PHA-75/25, 27%, was measured at 10 wk and 23^{o}C. The decrease was much larger than the decreases measured at 20 and 30 wk. The underlying reasons for this discrepancy are unknown. There was no appreciable change in the PDI values of both MB nonwoven with respect to temperature and duration.

Table 16: Change of number-average molecular weight and polydispersity index of nonwoven mulches (Study 5)

Mulches	**Retrieval time (wk)**	**Soil Temperature (^{o}C)**	**$M_n$$^{a, b}$ (kDa)**		**SE^{c}**	**PDI^{b,d}**	
MB-PLA	0	23	99.5	AB	1.7	1.28	G
	10	15	100.7	A	0.3	1.28	G
		20	97.2	ABC	0.3	1.28	G
		23	92.4	DE	0.2	1.29	F
	20	15	96.2	BC	2.3	1.28	G
		20	97.4	AB	0.6	1.28	G
		23	94.8	BCD	2.1	1.27	G
	30	15	92.3	CD	1.9	1.30	F
		20	92.2	DE	0.6	1.29	F
		23	71.5	FGH	7.6	1.36	DE
MB-PLA+PHA-75/25	0	23	75.8	EF	0.6	1.38	BCD
	10	15	69.4	FGH	0.2	1.35	E
		20	65.8	IJK	0.7	1.35	E
		23	55.8	K	0.4	1.42	AB
	20	15	68.8	FGHI	0.7	1.40	B
		20	69.3	FG	2.1	1.47	A
		23	67.9	GHIJ	0.5	1.27	G
	30	15	71.1	FG	0.7	1.37	CDE
		20	64.6	JK	0.5	1.38	BCD
		23	64.9	HIJ	6.2	1.41	BC

[a] Number-average molecular weight based on polystyrene standards. Mean values were rank transformed and untransformed values were calculated and reported using Fisher's Least significance difference in SAS 9.3(2012); [b] Mean values with no common letters are statistically different ($p<0.05$) ; [c]SE= Standard error of M_n; [d] PDI= polydispersity index of PLA component

6.4.3. EFFECT OF SOIL TEMPERATURE ON THE MORPHOLOGICAL CHANGE OF MELTBLOWN MULCHES VERSUS SOIL BURIAL DURING SOIL BURIAL

Table 17 displays the thermal properties of both MB mulches after 30 wk at three different soil temperatures—obtained via DSC. There were no considerable changes in the values of T_m (PLA and PHA) and T_c for either MB mulch. The value of T_g for MB-PLA did not change to an appreciable extent for all three temperatures. At soil temperature of 20^{o}C, MB mulches underwent a greater loss of amorphous content (ΔH_m), than at 15 and 23^{o}C (Table 16) after 30 wk of soil burial. At 23^{o}C, notable decreases of ΔH_c and ΔH_m occurred for MB mulches, thereby indicating the loss of crystallinity. MB-PLA+PHA-75/25 at 15^{o}C and 20^{o}C underwent a loss of T_g (for its PLA component) of 22% and 8%, respectively. The depolymerization of PHA in MB-PLA+PHA-75/25, determined from the value of ΔH_m, was higher at 20^{o}C than 15^{o}C. The percentage of crystallinity for the PLA component of MB mulches (X_c), vis-à-vis "as-received" mulch, at 23^{o}C increased. In sum, the small difference between the three soil temperatures reflects the small effect of soil temperature on the thermal properties of the MB mulches.

Table 17: Comparison of thermal properties of MB nonwoven mulches in Study 5 as a function of soil temperature, after 30 wk of soil burial

Soil temperature	Nonwoven mulches	T_m[a] (°C)	ΔH_m[b] (J/g)	T_g[c] (°C)	T_c[d] (°C)	ΔH_c[e] (J/g)	X_c[f] (%)
As-received	MB-PLA	167.8	52.0	61.5	101.5	28.5	25.1
15°C	MB-PLA	167.3	46.4	61.2	102.0	23.8	24.1
20°C	MB-PLA	167.1	33.9	62.1	102.6	13.2	22.1
23°C	MB-PLA	166.9	47.4	61.3	101.6	18.8	30.5
As-received	MB-PLA+PHA-75/25 (PLA)	166.6	38.5	64.7	81.9	16.4	23.6
	MB-PLA+PHA-75/25 (PHA)	139.5	0.9	ND[g]	ND	ND	ND
15°C	MB-PLA+PHA-75/25 (PLA)	165.7	33.1	47.2	82.9	4.6	30.4
	MB-PLA+PHA-75/25 (PHA)	142.1	0.5	ND	ND	ND	ND
20°C	MB-PLA+PHA-75/25 (PLA)	166.3	17.7	55.5	91.2	2.7	16.0
	MB-PLA+PHA-75/25 (PHA)	144.4	0.2	ND	ND	ND	ND
23°C	MB-PLA+PHA-75/25 (PLA)	165.1	31.7	66.0	87.4	1.2	32.6
	MB-PLA+PHA-75/25 (PHA)	144.3	0.4	ND	ND	ND	ND

[a] Melting temperature of first heating cycle ; [b] Enthalpy of fusion of first heating cycle ; [c] Glass-transition temperature of second heating cycle ; [d] Crystallization temperature of second heating cycle ; [e] Enthalpy of crystallization of second heating cycle ; [f] Percentage of crystallinity of PLA determined from Eqn.3. ; [g] ND=Not determined

6.4.4. FTIR-ATR SPECTROSCOPY ANALYSIS OF CHEMICAL STRUCTURE FOR NONWOVEN MULCHES

The change of chemical structure for mulches buried for 30 wk at three different soil temperatures was investigated via FTIR-ATR. Absorbance peaks at 1740-1759 cm^{-1} and at 3100-3750 cm^{-1} corresponding to C=O stretching and –OH stretching, respectively were evaluated. The extent of the decreased intensity of C=O stretching was slightly more pronounced for MB-PLA at 20 and 23^{o}C than at 15^{o}C (Fig.28).The shoulder peak, corresponding to –C=O stretching at 1740-1759 cm^{-1}, for MB-PLA at soil temperature of 20^{o}C was almost equivalent to 23^{o}C. The carbonyl stretching of MB-PLA+PHA-75/25 was higher at soil temperature 20^{o}C than at 23 and 15^{o}C (Fig.29). The hydroxyl stretching band for MB-PLA at 23^{o}C was larger than MB-PLA+PHA-75/25 (Figs.28 and 29). Therefore, the results of FTIR-ATR analysis suggests that hydrolysis occurred (similar to Study 3 reported in Chapter 3), with extent of hydrolysis being greatest under ambient greenhouse conditions (20^{o}C). The Norrish Type II reaction was not detected for either of MB mulch, determined from the absence of peaks at 1718 and 1585 cm^{-1} position corresponding to –C=C bond formation and carboxylic end group formation , in contrast to mulches undergoing simulated weathering (Chapter 8).

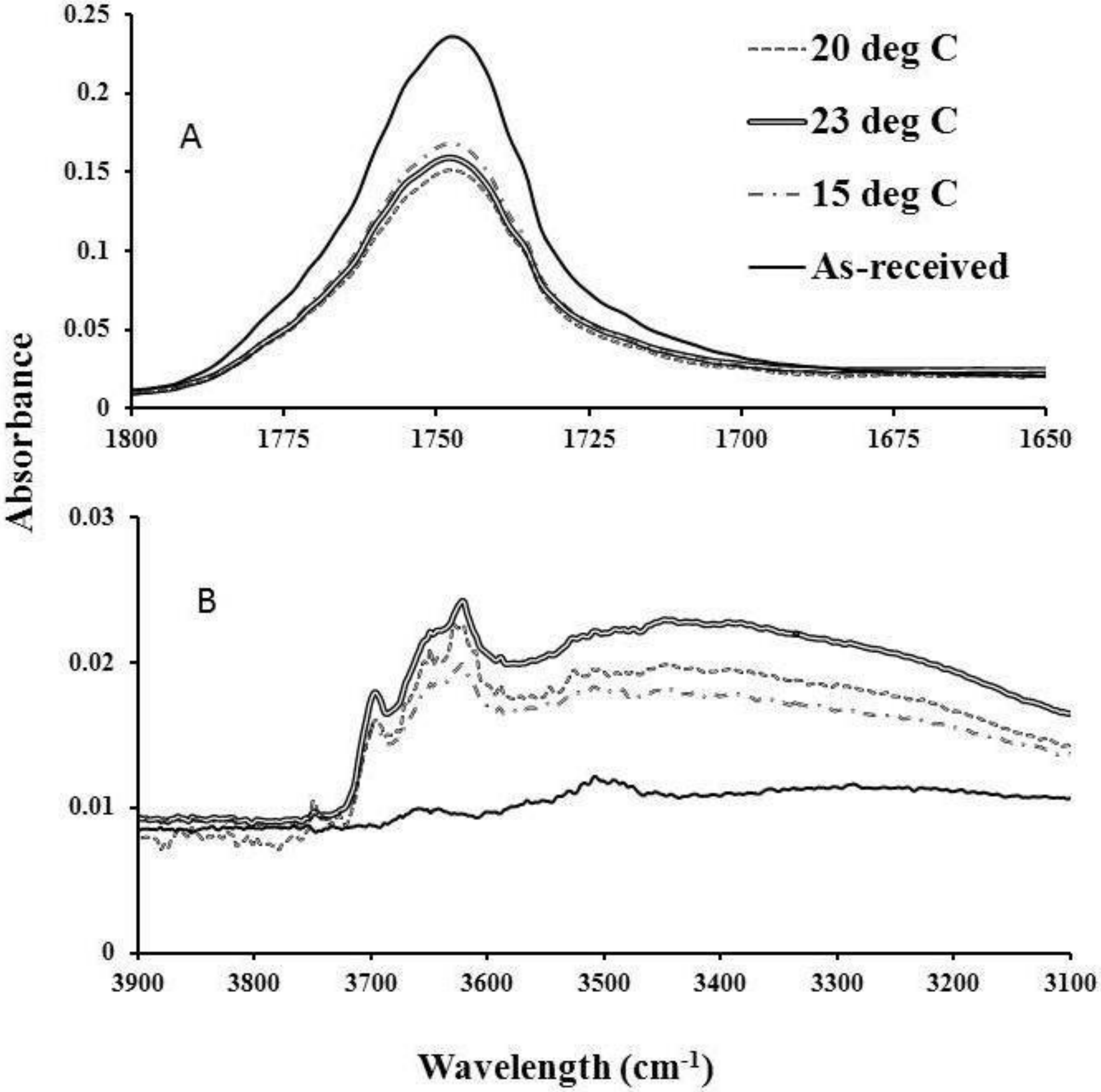


Figure 28: Effect of soil temperature on FTIR-ATR spectroscopic analysis of MB-PLA; A) C=O stretching band at 1740-1759 cm^{-1};B) -OH stretching band at 3100-3750 cm^{-1} (Study 5)

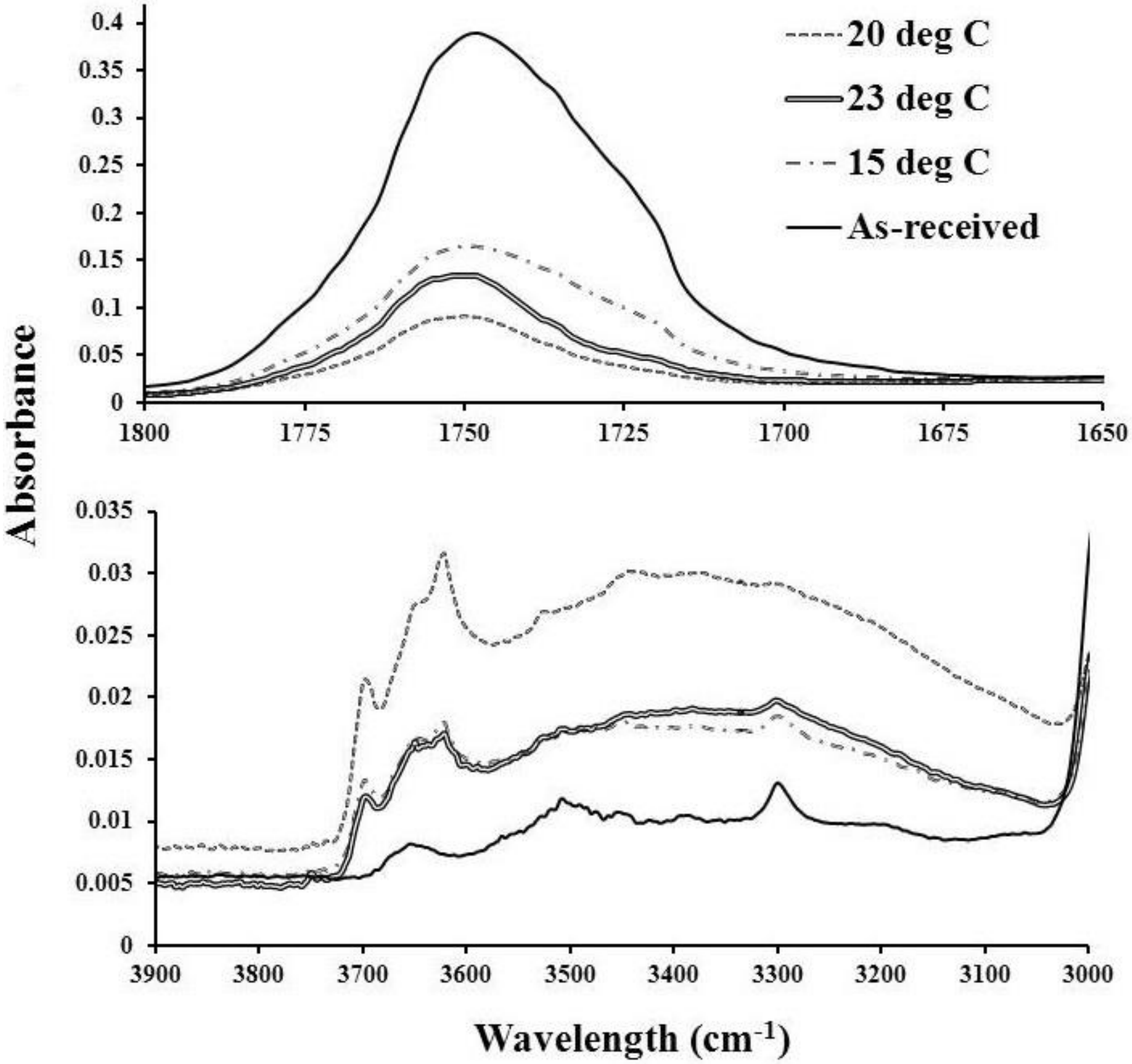


Figure 29: Effect of soil temperature on FTIR-ATR spectroscopic analysis of MB-PLA+PHA-75/25; A) C=O stretching band at 1740-1759cm^{-1} ; B) -OH stretching band at 3100-3501cm^{-1} (Study 5)

6.5. DISCUSSION

The effect of soil temperature on biodegradation of each MB mulch is discussed in detail below. It was presumed that an increase of biodegradation would occur with an increase of soil temperature. However, this hypothesis did not hold true for all situations.

6.5.1. EFFECT OF SOIL TEMPERATURE ON THE BIODEGRADATION OF MB-PLA

The biodegradation of MB-PLA at 3 different soil temperatures, 15°C, 20 °C, and 23 °C, was determined from the loss of tensile strength, depolymerization and changes of thermal properties. A hypothesis that MB-PLA would undergo less biodegradation at low soil temperature, based on Eqns. 5 and 6, is validated by the data. However, the biodegradation of MB-PLA was almost equivalent 20 and 23°C but was lower at 15°C. For example, the extent of hydrolysis for ester bonds [corresponding to the intensity of the C=O stretching region at 1740-1751 cm^{-1}] and formation of hydroxyl bonds [corresponding to the –OH stretching region at 3100-3501cm^{-1}] after 30 wk , determined from FTIR analysis, was almost equivalent at soil temperatures of 20 and 23°C but smaller at 15°C. Among the thermal properties, biodegradation of MB-PLA, determined from the loss of amorphous content (ΔH_m), was more pronounced at soil temperature 20 and/or 23°C than at 15°C. In addition, the loss of tensile strength of MB-PLA at 20°C and 23°C was almost equivalent. However, an inconsistent trend in the loss of tensile strength after 10 wk occurred for MB-PLA: the greatest loss of tensile strength was encountered at 15°C for an unknown reason.

The effect of three different soil temperatures on the depolymerization (via GPC analysis) of MB-PLA was in the following order, from the highest to the lowest level of biodegradation: 23°C > 20°C ≥15°C. The lowest soil temperature, 15°C, had a very little effect on thermal properties such as ΔH_c and T_g (or M_n, according to Eqn.4), of MB-PLA. Overall, results for the change of physico-chemical parameters for MB-PLA suggest that the elevated soil temperature (23°C) that simulated the warm environment did not effectively increase the soil temperature to a large extent.

6.5.2. EFFECT OF SOIL TEMPERATURE ON THE BIODEGRADATION OF MB-PLA+PHA-75/25

The loss of tensile strength, depolymerization and changes of thermal properties for MB-PLA+PHA-75/25 were compared at three soil temperatures (15, 20, and 23°C). Results generally support the hypothesis that high soil temperature enhances biodegradation. However, the difference between the summer-like, higher, soil temperature, 23°C, and the average soil temperature, 20°C, is small, which would lead to minor differences in the change of physico-chemical properties for the mulch between the two temperatures. To support, there was no statistical significance of the loss of tensile strength between 20 and 23°C (Fig.27). Additionally, after 30 wk, the soil temperature 23°C influenced the depolymerization of MB-PLA+PHA-75/25, determined by GPC, to a similar extent as at 20°C. In contrast, the decrease of T_g, T_c and ΔH_c were slightly higher at 20°C than at 23°C (Table 17). The winter-like, lower, soil temperature (15°C) led to a smaller extent of biodegradation for MB-PLA+PHA-75/25, presumably due to decreased microbial abundance. For example, the loss of tensile strength at 20 and 23°C was significantly higher than at 15°C after 10 wk (65%, 88%, and 94% loss at 15°C, 20°C, and 25°C, respectively) (Fig.28). In sum, after 30 wk of soil burial, the biodegradation of MB-PLA+PHA-75/25 occurred to an equal extent at 20°C and 23°C, but was lower at 15°C.

To improve the experimental design of Study 5, future research should employ elevated soil temperature of 35-40°C to understand the importance of elevated temperature on biodegradation. It is also recommended to conduct a soil burial study in a chamber with a more robust heating element/process control system for controlling the temperature to a desirable setpoint, instead of the heating pads employed in this study. At composting conditions i.e., > 58°C, PLA definitely undergo biodegradation confirmed by many studies [109, 123, 147], including Chapter 8 of this dissertation.

6.6. CONCLUSIONS

Study 5 elucidated the influence of soil temperatures (15, 20 and 23^{o}C) on biodegradation of MB mulches. The effects of soil temperatures, 23 and 20^{o}C, on the tensile strength of MB mulches were almost equivalent after 10 wk. The loss of tensile strength at 20 and 23^{o}C was higher for MB-PLA+PHA-75/25 than at 15^{o}C. In contrast, MB-PLA underwent greater loss of tensile strength at 15^{o}C than at 20 and 23^{o}C. After 30 wk, both of the MB mulches underwent a slightly higher extent of depolymerization at 20^{o}C and/or 23^{o}C than at15^{o}C. In conclusion, an increase of soil temperature from 20^{o}C to 23^{o}C did not strongly influence the biodegradation of MB mulches). Ambient soil temperature (20^{o}C) decreased the thermal properties, particularly X_c of both MB mulches to a greater extent than 23 and 15^{o}C. A decrease of soil temperature from 20^{o}C to 15^{o}C reduced the biodegradation of both MB mulches than 20 and 23^{o}C.

CHAPTER 7

SOIL BURIAL STUDY 6: KINETICS OF BIODEGRADATION FOR NONWOVEN MULCHES

7.1. INTRODUCTION

The rate and extent, hence the time scale, of biodegradation the mulches depends on the environmental conditions and the inherent physico-chemical properties of the plastic mulch: the type of biopolymer and processing type (e.g., film or fiber). The persistence of debris of biodegradable film or fiber is the main concern for mulches after useful service life. In this study, biodegradation kinetics of MB nonwoven mulches is reported. A previous study demonstrated that PDLLA film followed the first order degradation kinetics in water. This study will determine if the PLA-based nonwoven mulches described in Studies 2-5 follow the same reaction order. In addition, the kinetics for the decrease of tensile strength and chemical properties (molecular weight and thermal properties derived via DSC) will be measured and compared, to better understand the relationship between mechanical properties and chemical changes of the biopolymers, thereby leading to a better understanding of the mechanism of biodegradation (as per Fig.10 in Section 2.5.3).

7.2. OBJECTIVES

The objective of Study 6 is to understand the kinetics of biodegradation related parameters of MB nonwoven agricultural mulches buried in trays filled with soil and compost under high water delivery rate. The time course of biodegradation was characterized by the loss of tensile strength and number-average molecular weight.

7.3. EXPERIMENTAL

7.3.1. MATERIALS

Three nonwoven mulches were employed in this study:

1. MB-PLA
2. MB-PLA+PHA-75/25
3. SB-PLA-2011 (black)

The inherent properties and feedstock of the nonwoven mulches were provided in Table 4.

7.3.2. EXPERIMENTAL DESIGN

A completely randomized statistical design was used in Study 6. Unlike other studies in this dissertation, Study 6 was planned for 45 wk. The experiment, conducted in the North Bay Greenhouse on the UTIA campus, was started on February 23, 2013 and completed on December 13, 2013. There were eight retrieval times incorporated into experimental design and three replicates of each of the two MB mulches at each retrieval time employed. Data from the final retrieval time for the MB and SB mulches, December, 2013, have not been fully analyzed and will not be described in the dissertation. Therefore, the total number of plastic trays, of dimension 52 cm L x 25 cm W x 6 cm D, filled with soil and compost containing mulch were 54 [(2 MB mulches* 8 retrieval times * 3 replicates) + (1 SB mulch * 2 retrieval times * 3 replicates)]. Dewey silt loam soil, collected from USDA certified organic farm, was mixed with compost (Black kow). The amounts of soil and compost were given in Study 2. All units received a high water delivery rate (1000 mL per 48 hr)—trickled by a water can. The air and soil temperature of Study 6, determined by Waterscout SM 100sensors (Spectrum Technologies, Plainfield, IL, USA) was 25.17±0.95^{o}C and 24.39±1.57^{o}C, respectively. The average soil moisture was 12.52 ± 3.02% throughout the study determined by sensors.

7.3.3. EXPERIMENTAL METHODS

Experimental methods used to characterize the biodegradation of mulches consisted of the following:

I. Tensile strength testing: This method, discussed in detail in Section 3.3.1.3, was conducted between 0- 17 wk and 0- 22 wk for MB-PLA+PHA-75/25 and MB-PLA, respectively.
II. GPC: This method was discussed in Section 3.2.1.4.2

III. DSC: Q2000 calorimeter from TA Instruments (New Castle, Delaware, USA)—available in Polymer Characterization Laboratory (PCL) of Chemistry Department at UTK—was used to analyze the mulch samples. The procedure was provided in Section 3.2.1.4.3. This test was performed on one of the three replicates of MB-PLA+PHA-75/25 retrieved at each time. Mr.Tom Malmgren, PCL Manager, performed the DSC analysis.

IV. Analysis of variance (ANOVA) was conducted using mixed model using SAS 2013, V9.3 software, SAS Institute Inc., Cary, NC, USA. Mean values were calculated and compared using Fisher's Least Significance Difference method.

7.4. RESULTS

7.4.1. KINETICS FOR THE CHANGE OF TENSILE STRENGTH OF NONWOVEN MULCHES VERSUS BURIAL TIME

Fig.30 displays the tensile strength testing results for MB-PLA nonwoven mulches. The tensile strength of MB mulches, presumably due to biodegradation (Chapter 5), decreased significantly with burial time ($p<0.001$). Extreme defragmentation and deterioration limited the tensile strength testing of MB-PLA+PHA-75/25 to only 0-17 wk, whereas MB-PLA's tensile strength was tested for 0-22 wk (Fig 30). The tensile strength for MB-PLA+PHA-75/25 decreased by 80% at the end of 17 wk and 88% loss of tensile strength for MB-PLA at the end of 22 wk. The decrease of tensile strength of MB mulches was in accordance with the previous Studies 2-5.

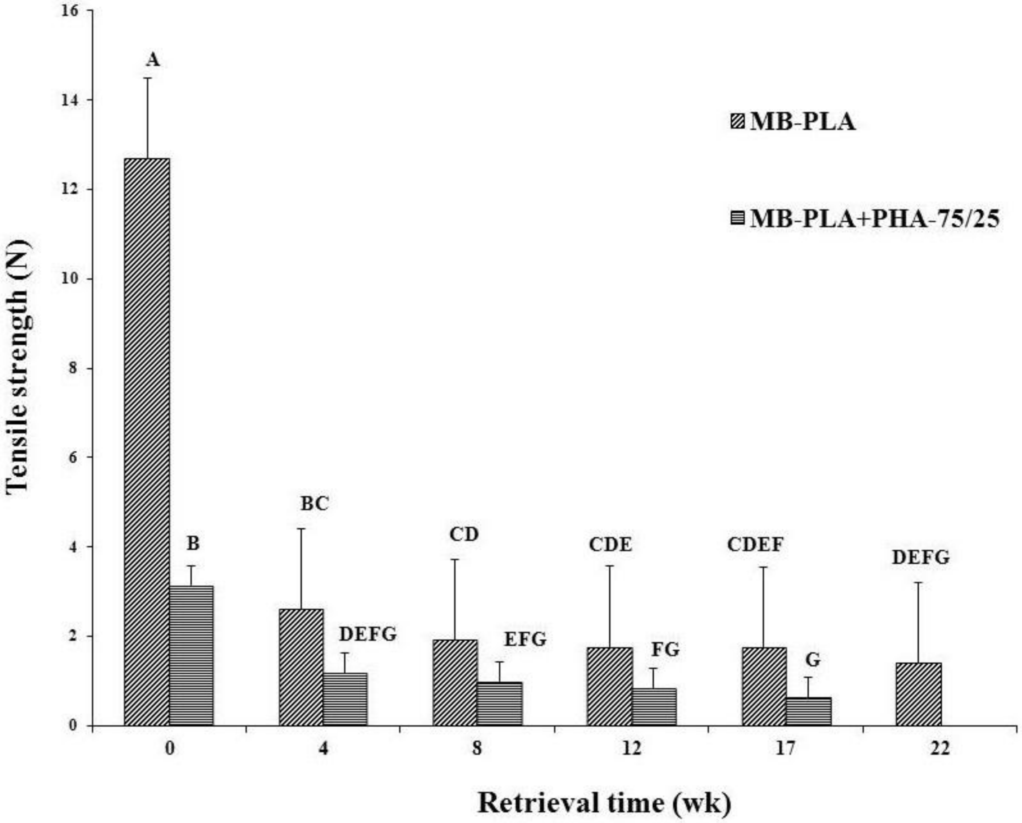


Figure 30: Decrease of tensile strength values of MB-PLA+PHA-75/25 and MB-PLA versus time (Study 6). Mean values represented by bars with no common letter groupings are statistically different.

The following equation is proposed to model the rate of tensile strength loss vs. time (-r, N s^{-1}) for biodegradation of MB mulches:

$$-r = k[TS]^{\alpha} \qquad \textbf{(7)}$$

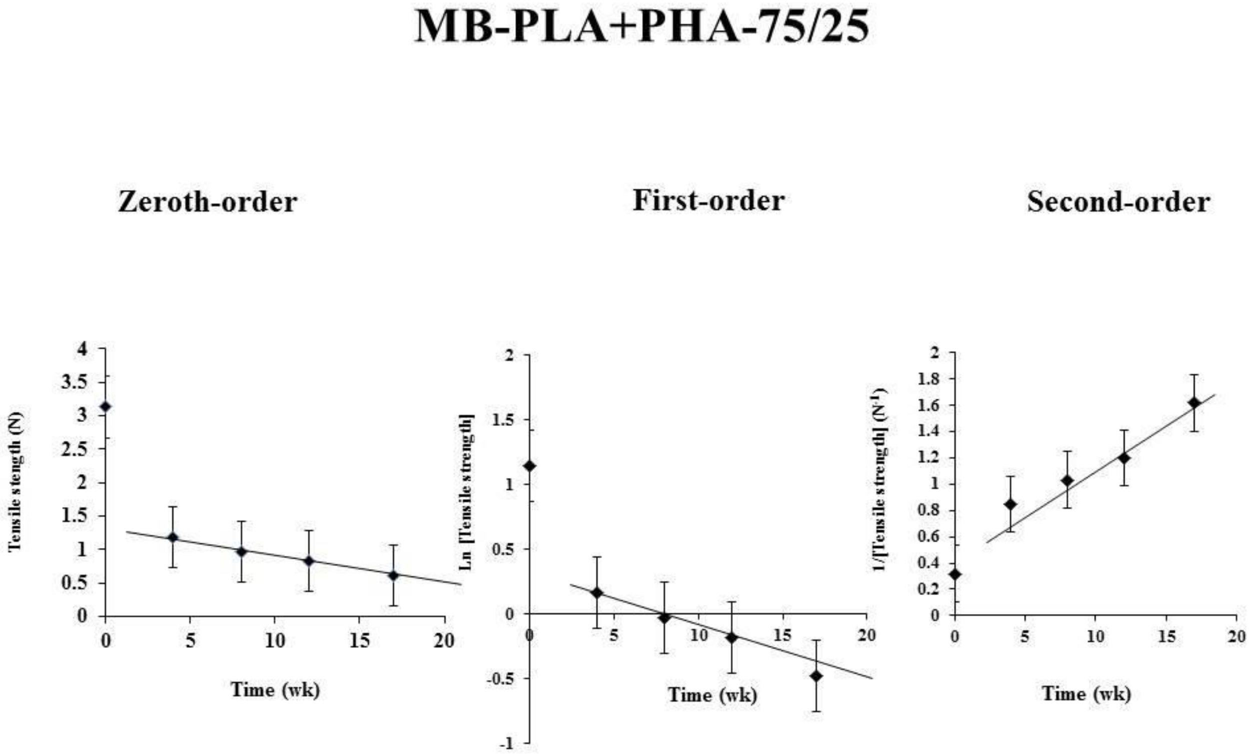
where k is the rate constant, [TS] is the tensile strength and α is the reaction order.

The linear plots of zeroth, first and second-order for MB mulches was obtained by plotting: the tensile strength vs. time , logarithm of tensile strength vs. time, and inverse of tensile strength vs. time, respectively (Figs.31 and 32) [162]. The reaction order for the loss of tensile strength as a function of time (either zeroth, first, or second) was obtained by comparing the best fit via linear regression (R^2 value) for the three plots described above. Values calculated for the rate constant (k), y-intercept, and R^2 for each of the three plots applied to tensile strength data for MB-PLA+PHA and MB-PLA are given in Table 18. Based on R^2 values, the loss of tensile strength for MB-PLA+PHA-75/25 followed zeroth-order reaction rate except between 0-4 wk (Fig.31), although the first-order fit to the data was also good. Because MB-PLA and MB-PLA+PHA nonwoven mulches were prepared using same PLA feedstock and almost exhibited similar physical properties such as weight, thickness and fiber diameter (Table 4), degradation kinetics for the former were also assumed to follow first-order kinetics. However, the reaction rate for MB-PLA followed second-order (Fig.32).Thus, the best fit, based on the R^2 values in Table 18, for MB- PLA and MB-PLA+PHA-75/25 were second-order and zeroth order degradation rate, respectively. Based on the values of k given in Table 18, MB-PLA+PHA-75/25 underwent a higher rate than MB-PLA.

Table 18: Linear regression to determine the reaction kinetics for the loss of tensile strength of MB nonwoven mulches (Study 6)

Mulch	Reaction order	Rate constant [d,e] (k)	Y-Intercept[c]	R^2
MB-PLA+PHA-75/25[a,c]	Zeroth	0.042 ± 0.002 ($N\ wk^{-1}$)	1.33 ± 0.03 (N)	0.99
	First	0.048 ± 0.003 (wk^{-1})	0.37 ± 0.04	0.99
	Second	0.058 ± 0.007 ($N^{-1}\ wk^{-1}$)	0.58 ± 0.08 (N^{-1})	0.97
MB-PLA[b,c]	Zeroth	0.055 ± 0.015 ($N\ wk^{-1}$)	2.58 ± 0.22 (N)	0.81
	First	0.029 ± 0.007 (wk^{-1})	0.98 ± 0.10	0.86
	Second	0.015± 0.003 ($N^{-1}\ wk^{-1}$)	0.36 ± 0.05 (N^{-1})	0.89

[a] Reaction-order fits were made on data collected between 4 and 17 wk only ; [b] Reaction-order fits were made on data collected between 4 and 22 wk only ; [c] The model fits for MB-PLA+PHA and MB-PLA were given in Figures 31 and 32, respectively; [d] Uncertainties given for rate constants and y-intercepts reflect standard errors; [e] Rate constants determined from slopes of plots indicated in Figures 31 and 32 of MB-PLA+PHA-75/25 and MB-PLA, respectively.


MB-PLA+PHA-75/25

Zeroth-order

First-order

Second-order

Figure 31: Zeroth, first and second-order plots to determine the reaction order and rate constant for the decrease of tensile strength encountered for MB-PLA+PHA-75/25 nonwoven mulch during soil burial (Study 6)

MB-PLA

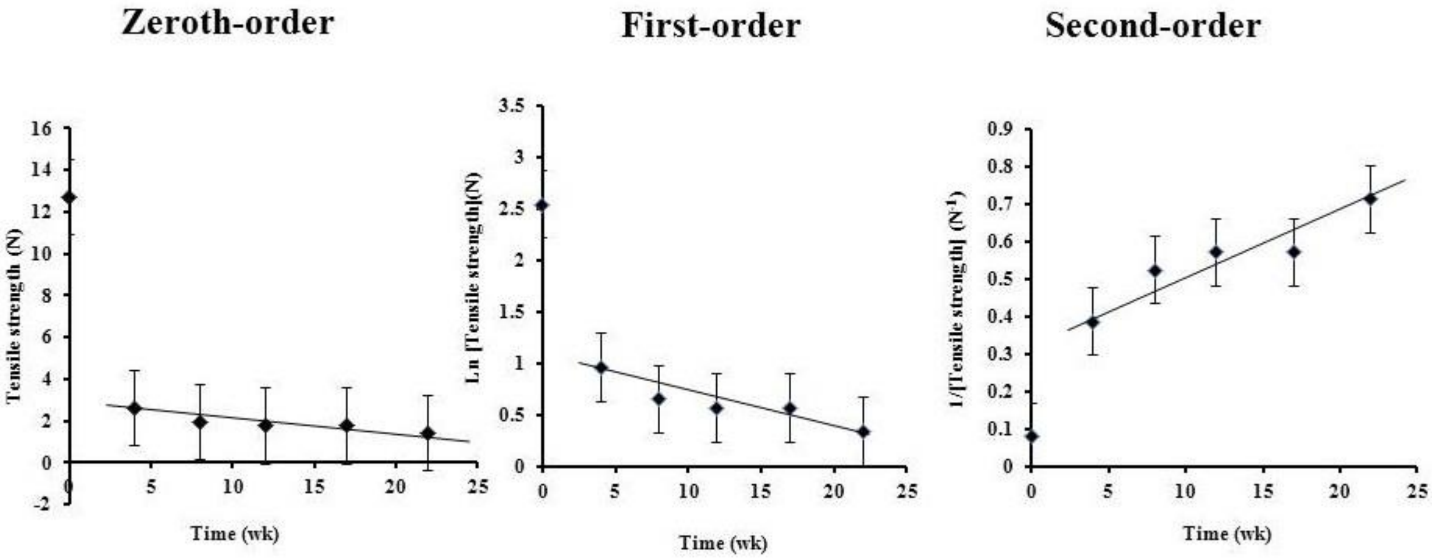


Figure 32: Zeroth, first and second-order plots to determine the reaction order and rate constant for the decrease of tensile strength encountered for MB-PLA nonwoven mulch during soil burial (Study 6)

7.4.2. KINETICS FOR THE CHANGE OF NUMBER AVERAGE MOLECULAR WEIGHT AND POLYDISPERSITY INDEX FOR NONWOVEN MULCHES VERSUS BURIAL TIME

Table 19 display the change of M_n and PDI values versus soil burial time for both MB mulches. The M_n of nonwoven mulches employed in Study 6 decreased significantly ($p<0.001$). MB-PLA underwent a notable M_n decrease (20%) only after 27 wk.

Table 19: Change of M_n and PDI versus time for PLA and PLA/PHA-based nonwoven mulches (Study 6)

Mulches	Retrieval time (wk)	M_n^{a,b} (kDa)		SE^{c}	PDI^{b,d}	
MB-PLA	0	99.5	A	1.7	1.28	HI
	4	94.0	B	0.3	1.28	HI
	8	95.1	B	1.3	1.28	I
	12	100.7	A	0.7	1.29	H
	17	99.3	A	0.5	1.33	F
	22	94.3	B	0.6	1.32	F
	27	79.5	D	0.3	1.30	G
	35	89.6	C	0.5	1.29	HI
MB-PLA+PHA-75/25	0	75.8	E	0.6	1.38	CD
	4	61.6	H	0.5	1.38	D
	8	69.8	F	0.8	1.38	D
	12	63.9	G	1.5	1.39	C
	17	61.4	H	0.9	1.45	A
	22	53.5	I	1.0	1.44	B
	27	42.6	K	1.1	1.45	A
	35	48.3	J	1.0	1.43	B
SB-PLA-2011	0	101.2	A	1.9	1.29	HI
	22	96.1	B	0.4	1.36	E

[a] Number-average molecular weight based on polystyrene standards, for PLA component of mulches only ; [b] Means are calculated and compared using SAS 9.3(2013).Mean values with no common letters reflect statistically significant ($p<0.05$) ; [c] Standard error; [d] polydispersity index of PLA with standard error <0.01

The decrease of M_n for MB-PLA+PHA-75/25 was the greatest (44%) after 22 wk. SB-PLA-2011 underwent a negligibly small decrease of M_n during 22 wk of soil burial, consistent with the minor changes in physico-chemical properties obtained for soil burial Studies 2, 3, and 5. PDI values for all of the nonwoven mulches increased slightly after buried for 12 wk, presumably due to bulk degradation of polymers, in agreement with results obtained for Studies 2-5.

The same approach described in the previous section to determine the reaction order and rate constant for the loss of tensile strength versus time was employed to obtain the reaction order and rate constant for the loss of M_n versus time) [162]. Among the proposed reaction orders for the M_n decrease versus time for MB-PLA+PHA-75/25, zeroth-, first,-, and second-order, the best linear fit was obtained for zeroth-order. Depolymerization of MB-PLA also followed zeroth- order kinetics. The zeroth-order reaction plots for both mulches are depicted in Figure 33, and values of k and other model-derived parameters are given in Table 20. Plots for the first- and second-order plots are not given. In contrast to the tensile strength kinetic models, which were employed on data taken for $\geq$ 4 wk of soil burial, kinetic modeling for M_n employed data for the entire time course of soil burial, including time zero. The rate of loss of tensile strength for both MB mulches was lower than the rate of loss of $M_{n.}$

Table 20: Parameters derived from a zeroth-order kinetic mathematical model applied to the loss of M_n versus time (Study 6)

Mulch	Rate constant, k (kDa wk^{-1})	Y-Intercept (kDa)	R^2
MB-PLA+PHA-75/25	0.74±0.21	70.4±4.3	0.79
MB-PLA	0.36±0.18	99.6±3.6	0.39

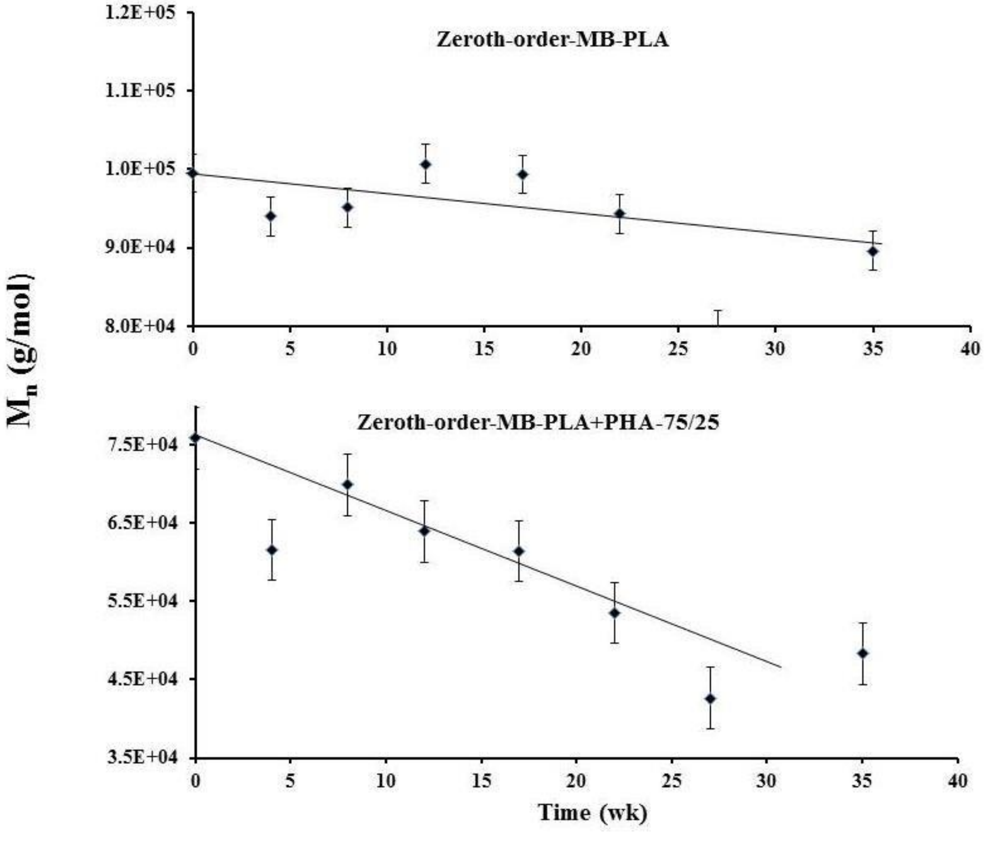


Figure 33: Zeroth-order kinetic plots for the loss of number average molecular weight (M_n) versus soil burial time, for MB-PLA and MB-PLA+PHA-75/25 mulches (Study 6)

7.4.3. MORPHOLOGICAL CHANGE OF MB-PLA+PHA-75/25 VERSUS BURIAL TIME

DSC was performed to determine the changes of thermal properties of MB-PLA+PHA-75/25 due to biodegradation. Table 21 displays the thermal properties of MB-PLA+PHA-75/25 determined from DSC. MB-PLA's thermal properties were not analyzed via DSC because of insignificant difference between "as-received" and soil buried mulches—as observed in Studies 2, 3, and 5.There was no considerable change of T_m for both PLA and PHA components. T_c of PLA also did not change appreciably. Because of thermal degradation for PHA in the first heating cycle, T_c could not be determined for PHA. T_g for PLA decreased from 64.7^{o}C to 38.7^{o}C after 22 wk. The loss of amorphous content PHA and PLA can also be determined from the decrease of value of ΔH_m. On comparing the enthalpy of crystallization (ΔH_c) for "as-received" and the mulch retrieved after 35 wk of soil burial, the value decreased by 98.8%—attributed to soil burial. The percentage of crystallinity for PLA component (X_c) of MB-PLA+PHA-75/25 increased from 23.6 to 37.4 after 35 wk of soil burial due to biodegradation of amorphous content.

Table 21: DSC results of MB-PLA+PHA-75/25 after each retrieval time

Retrieval Time (wk)	Component	T_m (°C)[a]	H_m (J/g)[b]	T_g (°C)[c]	T_c (°C)[d]	H_C (J/g)[e]	X_c (%)[f]
0	PLA	166.6	38.5	64.7	81.9	16.4	23.6
	PHA	139.5	0.9	ND[g]	ND	ND	ND
4	PLA	166.0	33.5	45.8	81.6	8.3	26.8
	PHA	142.1	0.5	ND	ND	ND	ND
8	PLA	166.3	33.0	47.0	82.8	11.9	22.6
	PHA	142.7	0.5	ND	ND	ND	ND
12	PLA	166.4	26.0	64.7	81.9	0.3	27.4
	PHA	144.9	0.2	ND	ND	ND	ND
17	PLA	165.9	32.4	47.5	82.9	5.5	28.8
	PHA	144.2	0.3	ND	ND	ND	ND
22	PLA	165.5	35.8	38.6	80.4	3.5	34.5
	PHA	143.1	0.3	ND	ND	ND	ND
27	PLA	165.6	33.6	42.7	81.7	1.5	34.3
	PHA	144.9	0.3	ND	ND	ND	ND
35	PLA	165.6	35.2	59.7	82.8	0.2	37.4
	PHA	145.4	0.3	ND	ND	ND	ND

[a] Melting temperature from first heating cycle ;[b] Enthalpy of fusion from first heating cycle ; [c] Glass-transition temperature from second heating cycle ; [d] Crysatllization temperature from second heating cycle ;[e] Enthalpy of crysatllization from second heating cycle ;[f] Percentage of crystallinity of PLA was determined using Eqn.3; [g] ND-Not determined

7.5. DISCUSSION

The main goal of Study 6 is to determine the biodegradation kinetics of MB-PLA and MB-PLA+PHA-75/25 during soil burial. It should be noted that Study 6 analyzed the kinetics of biodegradation only for the loss of tensile strength and number average molecular weight. The change of thermal properties, derived from DSC, during 22 wk of soil burial was too small to allow for kinetic modeling.

7.5.1. DEGRADATION KINETICS OF MB-PLA+PHA-75/25

Both the tensile strength and M_n loss of MB-PLA+PHA-75/25 underwent zeroth-order degradation kinetics. In other words, MB-PLA+PHA blends underwent microbial degradation regardless of the amount of mulch in the soil. The decrease of thermal properties, particularly T_g, is strongly related to with number average molecular weight (M_n) (Eqn.4-Fox-Flory Equation in Chapter 4,). Therefore, MB-PLA+PHA-75/25 undergoes biodegradation under ambient soil conditions to a significant extent. In addition, when simulated weathering was applied to this mulch (Chapter 8), it greatly enhanced the inherent biodegradability of the mulch (measured via ASTM D5388, biodegradability under composting conditions). Collectively, the results obtained via soil burial Studies 2-6 and simulated weathering provide a great deal of support for MB-PLA+PHA-75/25 to be recommended as a “Class II” biobased and biodegradable mulch material in ASTM WK 29802 (Section 2.7.1.1).

7.5.2. DEGRADATION KINETICS OF MB-PLA

Study 6 evaluated the degradation kinetics for the loss of tensile strength and M_n. Tensile strength loss of MB-PLA followed second-order kinetics overall. The biodegradation starts out quickly, undergoing a loss of 10 N in tensile strength during the first four weeks, and then slows down as the time progresses beyond 4 wk, resulting in a decrease of 1.9 N between 4 and 22 wk.

The M_n loss of MB-PLA followed zeroth order degradation (R^2=0.39, Fig. 33). Results of MB-PLA suggested that there was no direct correlation between the loss of tensile strength and loss of M_n. The trend observed in Study 6 may be due to the fact that the biodegradation of PLA under ambient soil conditions was slow, as reviewed in [109, 110].

Zhang *et al* investigated the hydrolysis of PDLLA films of varying thickness (347,351,430,433, 442,452, and 484 µm), prepared and processed by melt pressing, for 60 days [163]. PDLLA films were incubated in distilled water for 37°C. The loss of tensile strength and molecular weight, the latter assessed by measuring the intrinsic viscosity, were described by first-order degradation kinetics. In addition, the degradation rate constants for the PDLLA film varied from 0.0398 day^{-1} to 0.0216 day^{-1}. However, it is not clear if the rate constants provided by the authors were for the loss of tensile strength or molecular weight. In addition, authors did not provide a valid reason for the range of rate constants [163]. A similarity between the results of Zhang [163] and Study 6 was the steep loss of PDLLA's tensile strength during the initial period of the time course of depolymerization, which was not accompanied by an abrupt loss of molecular weight.

A review on polymer degradation mechanism, by Göpferich [164], explained that the biodegradation of PLA could be measured by depolymerization and tensile strength; however, the degradation environment was not clearly stated. In addition, it was also claimed that the greatest loss of tensile strength would occur at a short time before significant depolymerization. Thus, the kinetics for loss of tensile strength are not equivalent to kinetics for molecular weight loss for PLA polymer. Results of MB-PLA (loss of tensile strength and M_n) in Study 6 were in agreement with above-mentioned review. Zhang *et al* [163] and the review on polymer degradation mechanism [164] suggest that there was no relation between the loss of tensile strength and molecular weight. Results for MB-PLA strongly support the hypothesis (Fig.10), where the proposed loss of tensile strength was >50% but M_n loss was <20%.

7.6. CONCLUSIONS

Soil burial study 6 was conducted to evaluate the kinetics of biodegradation. The loss of tensile strength values of MB-PLA+PHA-75/25 followed the zero-order reaction kinetics, while MB-PLA followed second order reaction kinetics. The M_n loss for MB-PLA and MB-PLA followed the reaction kinetics of zero-order. After 22 wk, T_g for MB-PLA+PHA -75/25 underwent a 36% decrease. The change of thermal properties for MB-PLA+PHA-75/25, for example ΔH_m and T_g, reflect the depolymerization that occurred, observed via the decrease of M_n (Eqn.4 Fox-flory equation).MB-PLA+PHA-75/25 underwent a greater rate and extent of degradation compared to MB-PLA.

CHAPTER 8

EFFECT OF SIMULATED WEATHERING ON PHYSICO-CHEMICAL PROPERTIES AND INHERENT BIODEGRADATION OF PLA/PHA NONWOVEN MULCHES

8.1 INTRODUCTION

Mulching the agricultural field using polyethylene (PE) films was started in early 1950’s [7, 165] to control weeds, not to mention the added advantage of obtaining “micro-climate”, beneficial to crops [166] (discussed in Section 1.1). After harvesting, PE films, due to their poor biodegradability should be removed from field, to prevent their transformation into persistent debris that can harm wildlife, particularly fish, through their ingestion. Typically, the retrieved PE mulches are either incinerated or buried in the soil. Incineration of PE films is strictly prohibited by US Environmental Protection Agency (EPA) due to environmental pollution. Landfilling of mulches is not always permitted due to the concern for pesticides and herbicides that may be adsorbed onto the mulches, and is a poorly sustainable end-of-life alternative.

Biodegradable mulch films are employed in the agricultural field to circumvent the problems of PE films. Biodegradable mulch films at the end of their service life, which can exist in the form of debris, can be rototilled into soil before the beginning of next planting season, thereby eliminating labor costs for removal. However, embrittlement of biodegradable films before the harvesting of crops [during a service-life] is a concern, since degraded mulches do not serve as a barrier for weeds. In addition, the biodegradation of non-biobased additives in biodegradable films are not known completely. Materials originated from renewable resources such as plant, animal and marine are referred to as being *biobased* [85].

Although certified organic agriculture in Europe and Canada employ biodegradable (nonbiobased) mulches in the field, the US National Standard Organic Board (NOSB) only recently approved the use of biodegradable plastic mulches if they meet the following criteria [167]:

> They should be completely biobased, determined by ASTM D6866—a testing method that determine biobased contents in solid, liquid and gaseous samples using radiocarbon analysis.

> They should contain no prohibited products including petroleum-based aliphatic-aromatic copolymers and feedstock derived from genetically modified organisms.
>
> They should undergo at least 90% biodegradation in soil absolute or relative to cellulose in two years, as determined by ASTM D5988 or any other related international testing methods.

Prior to biodegradation in soil, agricultural mulches employed in the field can undergo a significant amount of environmental degradation. Abiotic factors such as solar radiation [particularly ultraviolet (UV) light], temperature fluctuations, moisture and oxygen cause the degradation during the service life in agricultural fields—referred to as *weathering* [168]. In order to determine the service life of plastics, most of the weatherability tests are carried out in severe outdoor testing conditions that represent subtropical or desert climates [field tests, as explained in Section 2.5.5.1]. The standard outdoor testing approaches are insufficiently robust to screen for the large of plastics that are being rapidly developed [simulation tests, as explained in Section 2.5.5.2]. Hence, laboratory-accelerated weathering—almost equivalent to outdoor testing conditions—has gained popularity [169]. Valuable information can be obtained from simulated weathering test; for instance, laboratory weathering demonstrated that cross-linking of PBAT films [Ecoflex®] occurred after exposure to UV light, revealing a major disadvantage of employing PBAT films [134] in the field.

In order to address the NOSB requirements, biobased nonwoven mulches employing biopolymers, PLA and PLA/PHA blends, were developed by Dr. Larry C. Wadsworth at the University of Tennessee using nonwoven textile processing. Chapters 3-7 describe the biodegradability of the unweathered nonwoven mulches under ambient soil conditions. In this chapter, the effect of simulated weathering on the physico-chemical properties of the mulches is examined. Additionally, the inherent biodegradability of weathered and "as-received" nonwoven mulches under composting conditions (ASTM D5388) was conducted. Research work explained in Chapter 8 is the first study that mimics the real field conditions such as exposure to sunlight, especially

UV light, on PLA-based nonwoven mulches and examines their inherent biodegradability before and after being weathered. This work is pertinent to new standard being developed for ASTM WK 29802 (Section 2.7.1.1), biodegradability of plastics in soil under ambient conditions.

8.2 EXPERIMENTAL

8.2.1. EXPERIMENTAL DESIGN

Four nonwoven mulches were chosen for this study to compare the effect of incorporation of PHA in the mulch (MB-PLA vs. MB-PLA+PHA-75/25), of color [SB- PLA-2010 (white) vs. SB-PLA-2011 (black)] and nonwoven type (SB-PLA vs. MB- PLA). All four mulches were subjected to simulated weathering for 21 days, with mulch samples also retrieved at 9 and 16 days to analyze the physico-chemical properties—loss of tensile strength and thermal properties, T_g in particular, depolymerization, and microfiber breakage. Biodegradability under composting conditions was investigated for “as-received” and mulches that underwent simulated weathering for 21 days using ASTM D5338.

8.2.2. MATERIALS

The description of mulches investigated in this study (SB-PLA-2010 (white), SB-PLA-2011 (black), MB-PLA and MB-PLA+PHA-72/25) and feedstock employed in their preparation are provided in Table 4. Mulches were stored at room temperature prior to use. Cellulose powder, utilized as a positive control in composting biodegradation tests, was purchased from Fluka (St. Louis, MO USA).

8.2.3. EXPERIMENTAL METHODS

8.2.3.1. SIMULATED WEATHERING

Simulated weathering was conducted in School of Packaging, Michigan State University (MSU) in the fall of 2012. Simulated weathering of the mulches (69 X 149 X 3 mm) by UV irradiation and water-spray was carried out according to the ASTM standard G155 [170] in an accelerated weathering chamber (Ci4000 Xenon Weather-Ometer, Atlas Material Testing Technology LLC, USA). The films were irradiated with UV radiation (Irradiance: 0.35 W/m^2.nm; Wavelength: 340 nm) at a black-panel temperature of 63°C for 102 min followed by 18 min under UV rays and water spray while the temperature decreased inside the weatherometer. This cycle was repeated 252 times for a total exposure of 504 h (21 days) [170].

8.2.3.2. WEIGHT AND THICKNESS

Weight ($g\ m^{-2}$) and thickness (m) of mulches before and after 21 days of simulated weathering were measured according to ASTM D5729 and D3776, respectively [171, 172]. Five-to-ten subsamples measuring 2.54 cm X 15.24 cm in the machine direction (MD) were cut from a mulch sample. However, MB mulch underwent significant deterioration during simulated weathering, according to visual observation; therefore, smaller, 2.54 cm X 10.16 cm (MD) dimensions were employed for preparing subsamples of all MB mulches.

8.2.3.3. SEM

The SEM procedure was explained in Section 3.3.4.4

8.2.3.4. TENSILE STRENGTH TESTING

The procedure for tensile strength testing was explained in Section 3.3.4.1

8.2.3.5. GEL PERMEATION CHROMATOGRAPHY

The GPC procedure was explained in Section 3.3.4.2

8.2.3.6. DIFFERENTIAL SCANNING CALORIMETRY (DSC)

The DSC procedure was explained in the Section 3.3.4.3

8.2.3.7. ATTENUATED TOTAL REFLECTION-FOURIER TRANSFORM INFRARED SPECTROSCOPY (ATR-FTIR)

ATR-FTIR spectra of the four mulches before and after 21 days of simulated weathering were acquired on a FT-IR (IR Affinity-1, Shimadzu Co., Tokyo, Japan) equipped with a single reflection ATR system (MIRacle ATR, PIKE Technologies, Madison, WI USA). A resolution of 4 cm^{-1} and 32 scans were used for measuring of the spectrum. FTIR-ATR data was collected by Dr. Elodie Hablot, Postdoctoral Research Associate at MSU.

8.2.3.8. BIODEGRADABILITY TESTING UNDER COMPOSTING CONDITIONS

Biodegradation under composting conditions for the four mulches before and after 21 days of simulated weathering was tested in a controlled experimental environment for a 90 day period at MSU. The experimental setup was based on procedures outlined in ASTM D5338. Three-month-old mature compost (C/N ratio of 16.5) was obtained from MSU composting facility. The compost was size-reduced through a 5 mm sieve and inorganic materials such as glass, stones, and metals were removed. Dry compost (400 g) was mixed with 100 g of dry vermiculite, and the moisture level was adjusted to 60% of water holding capacity. The vermiculite (grade number 4 soil conditioner; Therm-O-Rock, New Eagle, PA, USA) provided aeration and moisture retention. Subsamples of the mulches (9 g) were cut into 1 X 1 cm squares and then added to 275 g of active compost in 2-L glass jars and incubated at 58°C for 90 days. No fresh compost was added to the bioreactors during the 90 day biodegradation period. The system consisted of 20 bioreactors: two references (i.e., containing no plastics), two positive controls of cellulose and two for each of the four mulches before and after weathering.

The average % biodegradation vs. time data collected for each mulch was simulated using a Loess' function in R, a locally weighted polynomial regression model. The smoothness of the loess fit depends on the specification of the number of observation used in each local fit (neighborhood). Twenty percent of the data were used for each local fit. Residuals were assumed to be identically distributed and described by a Gaussian distribution [173, 174]. The standard error variance is estimated from the sum of the residuals divided by its degrees of freedom. Confidence intervals (95%) are computed by adding or subtracting the standard error variance to the estimated value of the % biodegradation. Dr. Elodie Hablot collected the biodegradability data and performed the simulation using the Loess function.

8.2.3.9. STATISTICAL ANALYSIS

A completely randomized design was used to study the effect of weathering on tensile strength. A mixed model analysis was performed using SAS (2013,V9.3, SAS Institute Inc., Cary, NC USA). Mean values were calculated and compared using Least Significance Difference method

8.3. RESULTS

8.3.1. EFFECT OF SIMULATED WEATHERING ON WEIGHT, THICKNESS, AND FIBER DIAMETER OF MULCHES

Table 22 shows the effect of simulated weathering on the average dry weight per unit area and thickness. Simulated weathering of mulches led to an increase of weight, for most of the mulches, believed to reflect the adsorption of moisture. However, there was an exception. For instance, dry weight per unit area of MB-PLA+PHA-75/25 remained the same after 21 days weathering.

Table 22: Effect of simulated weathering treatment on the dry weight, thickness, and average fiber diameter of nonwoven agricultural mulches

Mulch	Weathering Time (days)	Dry weight per Area (g m^{-2})[1,2]	Thickness (μm)[2,3]	Fiber Diameter (μm)[2,4]
SB-PLA-2010	0	83.5±6.9	629 ±26	14.9 ± 0.3
	21	94.8	734	14.8 ± 0.3
SB-PLA-2011	0	75.6±5.2	608±45	15.8 ± 0.4
	21	80.3	636	14.7 ± 0.4
MB-PLA	0	79.6±0.6	687±6	7.5 ± 0.6
	21	85.4	743	7.3 ± 0.4
MB-PLA+PHA 75/25	0	80.1±0.8	570±6	15.3 ± 0.6
	21	79.9	595	13.6 ± 0.8

[1] via ASTM D3776 [175] ; [2] uncertainty range given for the reported values reflect standard error, [3] via ASTM D5729 [171] ; [4] via scanning electron microscopy (SEM);

8.3.2. EFFECT OF SIMULATED WEATHERING ON FIBER BREAKAGE

SEM micrographs of mulches were taken before and after 21 days of simulated weathering (Fig.34). The fiber breakage of MB-PLA+PHA-75/25 occurred to a greater extent than MB-PLA after 21 days simulated weathering. The durable SB mulches did not encounter fiber breakage after 21 days simulated weathering (figure not shown).

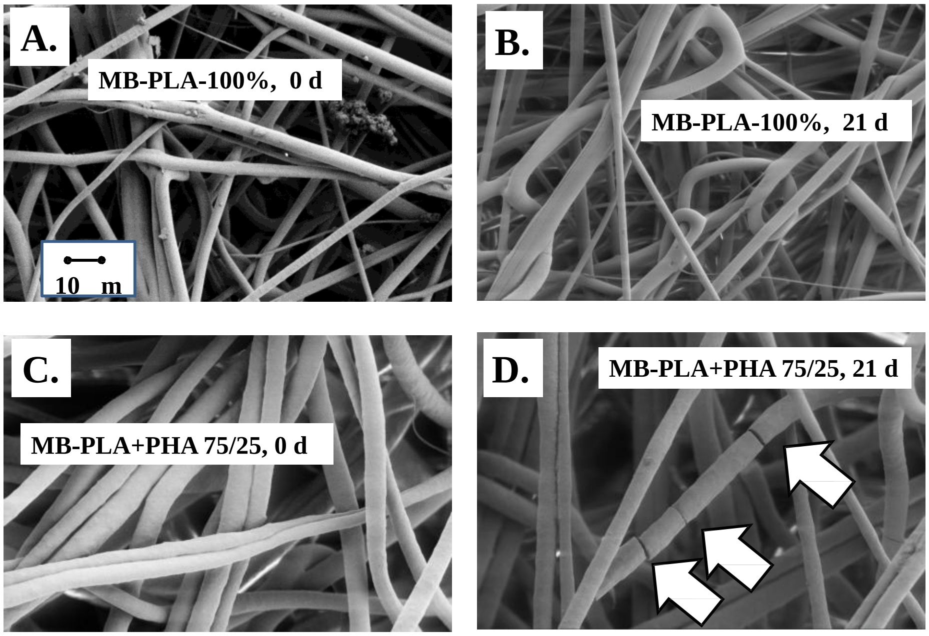


Figure 34: SEM micrographs of MB-PLA and MB-PLA+PHA-75/25 before and after21 days simulated weathering

8.3.3. EFFECT OF SIMULATED WEATHERING ON TENSILE STRENGTH

Table 23 compares the tensile strength value of “as-received” mulches and mulches that were exposed to 21 days simulated weathering. The “as-received” SB-PLA mulches displayed the highest tensile strength (~50 N) consistent with the larger fiber diameters of SB vs. MB materials. The tensile strength value of “as-received” MB-PLA and MB-PLA+PHA-75/25 mulches were 9 N and 4 N, respectively. Commercial PE and biodegradable films showed 8-12 N of tensile strength [85]. MB mulches displayed a larger decrease in tensile strength than SB mulches due to simulated weathering. The maximum loss, 95%, was observed for MB-PLA+PHA-75/25 after 21 days of simulated weathering, whereas MB-PLA underwent only ~50% loss of tensile strength value. The marginal (14%) decrease of tensile strength value for SB-PLA-2010 indicated the recalcitrance of SB mulches to simulated weathering. The loss of tensile strength values for SB mulches due to simulated weathering coincided soil burial Study 3—tensile strength loss was higher for SB-PLA-2010 (white) (10%) than SB-PLA-2011 (black) (3%).

Table 23: Effect of simulated weathering on the tensile strength of nonwoven agricultural mulches

Mulch	Weathering Time (days)	Tensile strength mean (N)[1]
SB-PLA-2010 (white)	0.0	56.21 ± 2.11 a
	8.5	46.02 ± 13.48 abc
	16.5	34.96 ± 1.36 c
	21.0	47.61 ± 8.25 b
SB-PLA-2011 (black)	0.0	37.12 ± 3.84 c
	8.5	42.52 ± 15.57 abc
	16.5	46.71 ± 6.53 abc
	21.0	39.60 bc
MB-PLA	0.0	8.96 ± 2.23 d
	8.5	3.68 ± 0.27 de
	16.5	4.66 ± 0.67 de
	21.0	4.12 ± 1.15 de
MB-PLA+PHA- 75/25	0.0	3.90 ± 0.09 de
	8.5	0.71 ± 0.11 de
	16.5	0.29 ± 0.09 de
	21.0	0.21 ± 0.27e

[1] Mean values ± standard error compared using Fisher's Least significant difference (LSD) in SAS software. Means with no common letters are statistically different ($p<0.05$)

8.3.4. EFFECT OF SIMULATED WEATHERING ON MOLECULAR WEIGHT AND POLYDISPERISTY INDEX OF NONWOVEN MULCHES

Table 24 provides M_n and PDI values for “as-received” and mulches that were exposed to simulated weathering. The similarity in the values of M_n and PDI of SB and MB mulches was due to their common PLA feedstock (Table 5). A prominent decrease of M_n (~32%) occurred for MB-PLA+PHA-75/25 after 21 days of weathering. Among SB mulches, SB-PLA-2011 (black) underwent the greatest decrease of M_n (10%). MB-PLA displayed least decrease of M_n after 21 days (3%); however, 9% loss of M_n was observed after 16.5 days of weathering. There were no notable changes of molecular weight distributions (PDI) for MB and SB mulches prepared from 100% PLA before and after simulated weathering. However, there was 8% increase of PDI for MB-PLA+PHA-75/25, presumably due to bulk degradation.

Table 24: Effect of simulated weathering duration on M_n and PDI of PLA in nonwoven agricultural mulches

Mulches	Weathering Time (days)	$M_n^{1,2}$ (kDa)	PDI of PLA^{2,3}
SB-PLA-2010 (white)	0.0	130 ± 1	1.28 ± 0.00
	8.5	127 ± 1	1.28 ± 0.01
	16.5	128 ± 1	1.28 ± 0.00
	21.0	128 ± 1	1.28 ± 0.00
SB-PLA-2011 (black)	0.0	101 ± 2	1.29 ± 0.01
	8.5	100 ± 1	1.28 ± 0.00
	16.5	98.8 ± 0.2	1.29 ± 0.01
	21.0	91.6 ± 0.8	1.28 ± 0.01
MB-PLA	0.0	99.5 ± 1.7	1.28 ± 0.00
	8.5	102 ± 5	1.29 ± 0.00
	16.5	90.8 ± 1.1	1.28 ± 0.00
	21.0	96.4 ± 0.5	1.27 ± 0.00
MB-PLA+PHA- 75/25	0.0	75.8 ± 0.5	1.39 ± 0.01
	8.5	78.2 ± 5.2	1.39 ± 0.01
	16.5	53.5 ± 1.7	1.45 ± 0.03
	21.0	51.4 ± 0.2	1.51 ± 0.01

[1] Based on comparison to polystyrene standards; [2] the data were not normally distributed; hence, a rank transformation was performed. The untransformed means with respective standard errors are reported; [3] polydispersity index

8.3.5. EFFECT OF SIMULATED WEATHERING ON THERMAL PROPERTIES OF MULCHES

DSC was used to determine the thermal properties of nonwoven mulches before and after simulated weathering. Results are displayed in Table 25. “as-received” nonwoven mulches (SB-PLAs and MB-PLAs) exhibited similar thermal properties i.e., T_g and T_m of PLA were in the range of 62-67 and 162-168^{o}C, respectively. This was primarily due to same feedstock being used in the preparation of the mulches [with the exception of SB-PLA-2010 (white)]. The addition of PHA decreased the melting enthalpy of PLA, particularly for “as-received” MB-PLA+PHA-75/25. In addition, the effect of simulated weathering on MB-PLA+PHA-75/25 was very prominent leading to decrease the T_g from 65^{o}C to 57^{o}C. This result reflects the decrease of molecular weight, crystallization enthalpy (ΔH_c), and fiber breakage of MB-PLA+PHA-75/25 during simulated weathering, as discussed above. In contrast, the increase of $T_{g,}$ ΔH_m, and ΔH_c of SB-PLAs indicated the structural reorganization of the polymer molecules.

Table 25: Effect of simulated weathering treatment on the supramolecular structure of nonwoven agricultural mulches as determined by DSC

Mulch	Weathering Time (days)	T_m $(^{o}C)^{3}$	H_m $(J/g)^{3}$	T_g $(^{o}C)^{3}$	T_c $(^{o}C)^{4}$	H_c $(J/g)^{4}$
SB-PLA-2010 (white)	0.0	163	40	67	113	28
	21.0	163	45	72	115	31
SB-PLA-2011 (black)	0.0	164	53	64	97	22
	21.0	163	57	74	99	28
MB-PLA	0.0	168	50	66	101	31
	21.0	167	44	67	98	25
MB-PLA+PHA 75/25 (values for PLA)	0.0	166	38	65	82	17
	21.0	166	33	57	78	10
MB-PLA+PHA 75/25 (values for PHA)	0.0	139	1.2	ND[5]	ND	ND
	21.0	142	0.7	ND	ND	ND

[1] Values given are for PLA unless indicated otherwise; T_m = melting temperature, ΔH_m = melting endotherm, T_g = glass transition temperature, T_c = crystallization temperature, H_c = crystallization endotherm; [3] determined from first thermal cycle (cf. Figure 2); [4] determined from first plus second thermal cycle (cf. Figure 2); [5] Not determined

8.3.6. FTIR-ATR SPECTROSCOPY ANALYSIS OF NONWOVEN MULCHES BEFORE AND AFTER SIMULATED WEATHERING

The modification of chemical structure was determined by FTIR-ATR spectroscopy analysis. Band assignments corresponding to PLA are provided in Table 27.

Table 26: FTIR band assignment for poly (lactic acid) component of the nonwoven mulches [44, 125]

Wavenumber, cm^{-1}	Band Assignment
1759	—C=O carbonyl stretch
1460	—CH_3 bend
1382, 1362	—CH— deformation including Sym. and asym. bend
1267	—C=O bend
1194, 1130, 1093	—C—O— stretch
1085	—OH bend
926, 868	—C—C— stretch

Fig.35 provides the Norrish Type II reaction mechanism of ester bond cleavage due to photodegradation, particularly to exposure by ultraviolet (UV) light [176].

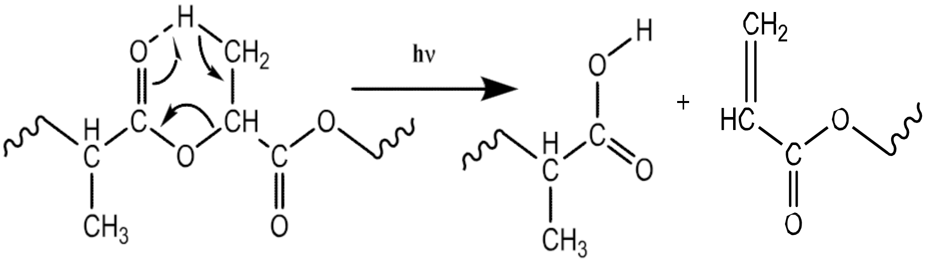


Figure 35: Reaction mechanism of Norrish Type II for the photodegradation of PLA

The Norrish Type II reaction, as shown in Fig.35, was reported to produce free carboxylic groups. The reaction takes place at ester group and ethylidene group adjacent to ester oxygen, as depicted in the Fig.35.

The addition of PHA in the mulch introduced the two important major changes in the neat PLA spectra (Fig.36): (i) carbonyl stretching (-C=O) at 1759 cm^{-1} became broader and peak was less intense; and (ii) -CH- deformation and C=O bending became more intense at 1300 cm^{-1} and 1267 cm $^{-1}$, respectively.

Simulated weathering induced the following changes, attributed to a Norrish Type II reaction (Fig.35): (i) a new peak at 1585 cm^{-1} is formed suggesting C=C- bond formation (consistent with Fig.35); (ii) the appearance of peak at 1718 cm^{-1}can be due to formation of carboxylic acid end group; (iii) the peak for ester -C=O– stretching decreased marginally; and (iv) the new peak formation corresponding to hydroxyl stretching region at 3370 cm^{-1} –the possibility of formation of peroxides and –OH end groups.

When comparing to the soil burial studies, there were two new shoulders in the mulches that underwent simulated weathering: one at 1585 cm^{-1} corresponding to C=C- bond formation and the other at 1718 cm^{-1} corresponding to carboxylic acid end group. This strongly supports the occurrence of photodegradation during simulated weathering. In Studies 2 and 5, there were no peaks at 1585 and 1718 cm^{-1} presumably due to absence of UV light penetration through the top layer of soil.

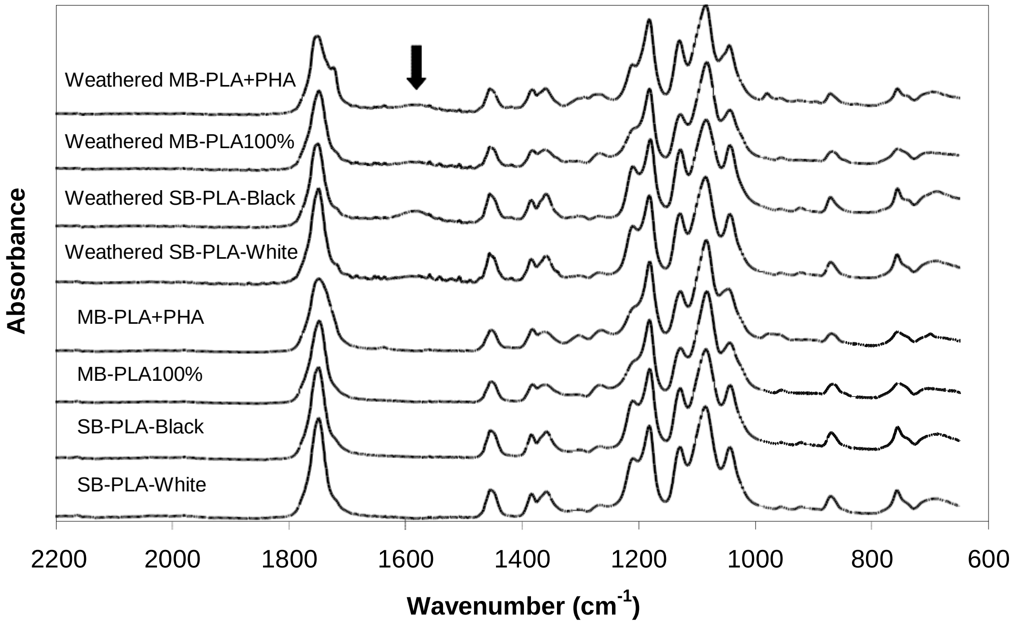


Figure 36: FTIR-ATR spectra of "as-received" mulches, and after 21 days of simulated weathering. The arrow shows the appearance of a peak at 1585 cm^{-1}, corresponding to C=C bonds and indicating the chemical structure change of mulches.

8.3.7. EFFECT OF SIMULATED WEATHERING ON BIODEGRADABILITY

The testing method ASTM D5338 was used to measure and compare the biodegradation of "as-received" and the nonwoven exposed to simulated weathering, with cellulose powder as a positive control for 90 days. A synopsis of results inferred from Fig.37are given below.

The rate of biodegradation for MB-PLA+PHA-75/25 was the highest (Fig.37) among the "as-received" mulches; however, it reached a plateau at 60 days. The final extent of biodegradation of "as-received" MB-PLA+PHA-75/25 was 67%. The rate of biodegradation of MB-PLA+PHA-75/25 that underwent simulated weathering was higher than any other nonwoven mulches used in this study. Moreover, the biodegradation of MB-PLA+PHA-75/25 underwent similar time course as the positive control, cellulose. The final extent of biodegradation of MB-PLA+PHA-75/25, simulated weathering exposed, was 91% (Fig.37).

As observed in Fig.37, MB-PLA exposed to simulated weathering achieved the highest extent of biodegradation (93%) and a rate of biodegradation that was similar to MB-PLA+PHA-75/25. The final extent of biodegradation of “as-received” MB-PLA was 80%, a significantly higher extent than the value achieved for MB-PLA+PHA-75/25 (Fig.37).

The final extent of biodegradation of SB-PLA-2011 exposed to simulated weathering and “as-received” was similar (~70%). The final extent of the white-colored “as-received” SB-PLA-2010 was the lowest among the mulches (~55%). Simulated weathering greatly enhanced the extent of biodegradation for SB-PLA-2010 to 72% (Fig.37). There was no significant effect on biodegradation due to the black vs. white color of SB mulches. Although SB mulches underwent less biodegradation than MB mulches, the inherent biodegradation requirements of the ASTM D6400, *Standard Specification for Labeling of Plastics Designed to be Aerobically Composted in Municipal or Industrial Facilities* (Section 2.7.1.2 and Fig.11), were met for both materials (≥ 60% biodegradation in 90 days, for both weathered and “as-received” mulches).

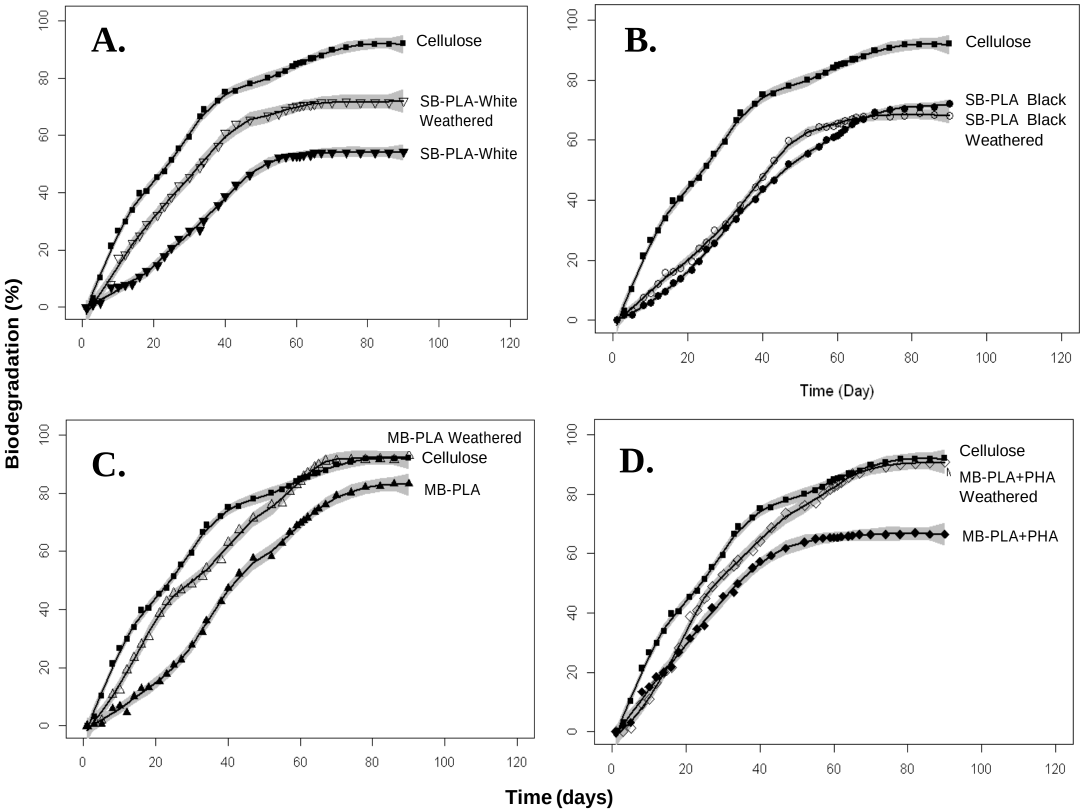


Figure 37: Biodegradation of cellulose powder compared to "as-received" and weathered A. SB-PLA-White, B. SB-PLA-Black, C. MB-PLA, and D. MB-PLA+PHA 75/25

8.4. DISCUSSION

The objective of this study is to determine the effect of simulated weathering on physico-chemical properties and biodegradability of nonwoven mulches under composting conditions (ASTM D5338). Additionally, the color of the mulches (white vs. black), inclusion of PHA (PLA vs. PLA+PHA) in the mulches and two different types of nonwoven (SB vs. MB) were compared. It is anticipated that after simulated weathering of 504 h (or 21 days) — which simulated the effect of photodegradation—white color SB mulches and MB- PLA+PHA blends would undergo greater extent of depolymerization and mechanical weakening than black-colored SB and MB-PLA-based nonwoven mulches. These topics are discussed in further detail below

8.4.1. SPUNBOND WHITE vs. BLACK COLOR NONWOVEN MULCHES

Previous studies have reported that white colored mulches undergo greater biodegradability than black colored mulches [134]. The loss of tensile strength of white SB mulches, relative to SB-PLA-2011(black), partially validated the hypothesis. However, there was no significant loss of molecular weight for both SB mulches (Table 23). Besides, both SB nonwoven mulches after simulated weathering underwent biodegradation to a similar extent (~65%) in ASTM D5338 (Fig.37).

8.4.2. MB-PLA vs. MB-PHA+PLA BLENDS NONWOVEN MULCHES

Inclusion of PHA in the MB nonwoven mulches increased the rate and extent of deterioration due to abiotic weathering—determined from the steep loss of tensile strength and molecular weight. In ASTM D5338, both the MB mulches after simulated weathering achieved a similar extent of biodegradation (>90% in 90 days). As-received MB-PLA (83%) underwent greater biodegradation than MB-PLA+PHA (63%). It should be noted that PHA is a generic name for P (3HB-co-4HB) (explained in Section 1.3.2). Maiti *et al.* compared the biodegradation of poly(3-hydroxybutyrate) or P(3HB) in compost at 60^{o}C to 30 ^{o}C and concluded that lower concentration of microorganisms at 60^{o}C accounted for significantly less biodegradation (30%) than at 30^{o}C (70%) [177]. It would thus be possible at composting conditions, a lesser amount of microorganisms in the bioreactor led to the lower biodegradation of MB-PLA+PHA-75/25 (Fig.37).

A question that remains to be explored is how to increase the number of microorganisms in the bioreactor of controlled tests. It is speculated by the author of this dissertation that by replenishing the compost at regular intervals depending on period for tests, the biodegradation of “as-received” MB-PLA+PHA blends can be increased. After simulated weathering, the percentage of biodegradation for both MB mulches was similar because of their deterioration prior to ASTM D5338 test. Thus, MB-PLA+PHA-75/25 nonwoven mulch can potentially serve as a “Class II” mulch material according to ASTM WK 29802, moreover, a material that meets biodegradability related specifications after being exposed to environmental conditions (Section 2.7.1.1). Subsequently, MB mulches can also be recommended for National Standard Organic Board where the criteria are: materials should be completely biobased and undergo 90% biodegradation in two years via ASTM D5988. Although ASTM D5338 and D5988 differ in their soil temperature, Fig.37 shows the weathering greatly enhanced the inherent biodegradability of mulches.

8.4.3. SPUNBOND vs. MELTBLOWN NONWOVEN MULCHES

Both SB nonwoven mulches were refractory to simulated weathering and underwent relatively less biodegradation (>60% in 90 days) than both MB nonwoven mulches (>90%). Nevertheless, the biodegradation at composting conditions (>60% in 90 days) met the compostability standard ASTM D6400. After all, PLA is well known to function as a compostable polymer [86, 178, 179].Thus, SB nonwoven are suggested to use as row covers in agriculture.

8.4.4. SIMULATED WEATHERING vs. OUTDOOR EXPOSURE

One of the limitations of simulated weathering is the correlation to outdoor exposure. ASTM G155 is a generic test method that never replicates any outdoor environment perfectly compostable.

First, correlation between the variables, i.e., the ratio of angle of radiation to moisture or the combination of temperature and moisture prevailing in the environment should be known. Second, a Xenon Arc Weather-Ometer can create only a limited number of environmental variables such as UV light, high and low temperature, and water spray, in the form of moisture and relative humidity. Natural and artificial pollutants, corrosive environment, and winds are factors found in the natural environment that cannot be produced by weatherometery—also affect the plastics and play a crucial role in degradation. Gathering all the information for positive or negative correlations to simulate one specific environment is not possible because of the variability of the natural environment from year to year [180]. Hence, the exposure hours of plastics or mulches in weathering cannot be interpreted as the equivalent outdoor exposure. Nevertheless, it is suggested to compare nonwoven materials' degradation under simulated weathering and outdoor exposure abreast.

8.5. CONCLUSIONS

The physico-chemical properties and biodegradation at composting conditions (ASTM D5388) of nonwoven as a function of simulated weathering were investigated. Four different nonwoven mulches were examined, to allow for the effect of simulated weathering on color (SB-PLA-white and black) and biopolymer composition (MB-PLA and MB-PLA+PHA blends) as well as nonwoven type (SB vs. MB) to be evaluated. The loss of tensile strength for SB-PLA-2010 (white) was higher (15%) than SB-PLA-2011 (negligibly small loss), suggesting the white coloring enhanced the degradation via photolysis. However, the loss of M_n for SB-PLA-2011 (black) was higher (~10%) than SB-PLA-2010 (white) (~1.5%). Among SB mulches, SB-PLA-2010 (white) underwent greater biodegradation than SB-PLA-2011 (black) after simulated weathering. The robust SB mulches withstood simulated weathering, and under composting conditions, it underwent only ~ 70% biodegradation. The Norrish Type II reaction, the underlying mechanism of photodegradation for PLA, played a very vital role in degradation of SB and MB mulches, as detected by FTIR. The biodegradation of SB-PLAs met the standard requirements (ASTM D6400) (>69% in 90 days).

The effect of simulated weathering, on modifying the physico-chemical properties was higher for MB-PLA+PHA-75/25 than for MB-PLA. For instance, the tensile strength of MB-PLA+PHA-75/25 underwent a greater loss (94%) compared to MB-PLA (50%). Similarly, the M_n of MB-PLA+PHA-75/25 decreased from 75.8 kDa to 51.4 kDa (32%), whereas MB-PLA's M_n value decreased only by 3%. The change of thermal properties for both MB nonwoven reflects the changes of M_n. The decrease of ΔH_m of PLA and PLA+PHA blends correspond to the loss of amorphous content and depolymerization. Although the rate of biodegradation under composting conditions (ASTM D5338) for both MB nonwoven mulches, after 21 days simulated weathering, was similar, MB-PLA underwent a slightly higher extent of biodegradation (93%) than MB-PLA+PHA-75/25 (91%).

CHAPTER 9

CONCLUSIONS AND RECOMMENDATIONS

9.1 CONCLUSIONS

The findings of the soil burial studies and simulated weathering that mimic the real field conditions employing the PLA based nonwoven mulches [Chapters 3-8] are discussed below. In addition, the inherent biodegradability under composting conditions of “as-received” nonwoven mulches and after exposed to simulated weathering for 21 days are also discussed in detail below.

9.1.1 SPUNBOND (SB) PLA-BASED MULCHES (SB-PLA-100%)

SB-PLA-2010 (white) was employed in Study 3, whereas SB-PLA-2011 (black) was in Studies 2, 3, and 6. Results of biodegradation of SB nonwoven mulches under ambient soil conditions (Studies 2, 3,and 6) suggested that the SB mulches are under the first stage of biodegradation for 30 weeks (Section 2.5.3 and Fig.10), where > 50 % loss of tensile strength and > 20 % decrease of M_n were not encountered yet. In addition, it is required to conduct a soil burial study for 24-36 months when employing unweathered SB mulches. In Study 2, soil amendments (HWDR, LWDR, HWDR+PJ and LWDR+PJ) had a negligibly small effect on the degradation of SB mulches. The tensile strength values of SB-PLAs did not change appreciably after 30 wk of soil burial (Studies 3, 4, and 7). Among the thermal properties, X_c (percent crystallinity of PLA component) and T_m of SB mulch [regardless of color] were decreased to a greater and lesser extent than “as-received”—indicating the slight loss of crystallinity during soil burial (Studies 2, 3, and 6). The marginal degradation—loss of tensile strength, M_n, and thermal properties, particularly T_g—suggested that SB mulches, regardless of color, can be employed for long-term agricultural applications such as row covers (Studies 3,4 and 6). Particularly, SB-PLA-2011 (black) can suppress weeds and provide “microclimate”—decreasing soil temperature during summer and preventing water loss or maintaining the humidity in soil [15, 135-137]. In addition, it is economically viable that they perhaps may survive two harvesting seasons in the agricultural field.

In Chapter 8, both SB-PLAs (white and black) were subjected to simulated weathering for 21 days prior to biodegradability test under composting conditions

[ASTM D5338]. Simulated weathering had no influence on the physico-chemical properties (tensile strength and M_n) of both SB mulches. Although both of SB-PLAs that were exposed to simulated weathering underwent relatively less biodegradation under composting conditions (~67-70% for 90 days), the inherent biodegradability requirement contained within the compostability standard (ASTM D6400) requirements (>60% for 90 days) was encountered.

9.1.2 MELTBLOWN (MB) MULCH (MB-PLA-100%)

The biodegradation of MB nonwoven mulches, determined from loss of tensile strength and M_n, including thermal properties such as T_g,T_m, T_c, and X_c and validated the hypothesis (Fig.10 in Section 2.5.3) i.e., > 50 % loss of tensile strength and > 20 % decrease of M_n. Among the soil amendments employed in Study 2, MB mulches exposed HWDR+PJ underwent significant decrease of M_n; however, the tensile strength loss was inhibited by HWDR+PJ. The biodegradation of MB-PLA in Study 3 is greater than BioTelo, a commercially available and partially biobased mulch film, based on the percent loss of loss of tensile strength and M_n. Study 5 employed three different soil temperatures (15, 20, and 23^{o}C); at low temperature (~15^oC), the loss of tensile strength was higher than 20 and 23^{o}C. However, after 30 wk and at 23^{o}C, loss of M_n was higher than 15 and 20^{o}C. Study 6 illustrated that loss of tensile strength for MB-PLA underwent second-order reaction order, while M_n loss was zeroth-order reaction rate—suggesting slow biodegradation of MB-PLA.

In Chapter 8, simulated weathering was shown to decrease physico-chemical properties of MB-PLA–tensile strength (50%) and M_n (3%). The crystallinity of PLA was also decreased by simulated weathering; T_c decreased from 101 to 89^{o}C and ΔH_c decreased from 31 to 25 J/g. Among the mulches that underwent weathering and tested in ASTM D5338, weathered MB-PLA underwent greatest biodegradation (93%) compared to “as-received” MB-PLA (~84%).

9.1.3 EFFECT OF INCORPORATION OF PHA IN SB AND MB-PLA BASED NONWOVEN MULCHES (SB-PLA+PHA-80/20, MB-PLA+PHA BLENDS)

The inclusion of PHA in the SB nonwoven mulches increased the degradation to a small degree (12% loss of M_n) [Study 3 in Chapter 4]. Although loss of tensile strength—due to inclusion of PHA—for SB-PLA+PHA-80/20 was not statistically significant, it was relatively higher (12%) vis-à-vis SB-PLA (white and black) nonwoven mulches [Study 3]. There was no appreciable loss of thermal properties (T_g, T_m, and ΔH_m) for SB-PLA+PHA-80/20. However, the percent crystallinity of PLA in SB-PLA+PHA-80/20 mulches decreased to the greatest extent. Regardless of PHA inclusion, crystallinity (X_c) of PLA for all SB mulches decreased. Overall, the inclusion of PHA in SB mulches had a very little effect on biodegradation.

The incorporation of PHA in MB-PLA mulches increased the biodegradation significantly. For instance, MB-PLA+PHA blends, employed in Studies 2-6, underwent greatest decrease of tensile strength (94%). The thermal properties examined in all the soil burial studies (2-6) indicated the decrease of crystallinity (X_c) for PLA in MB-PLA+PHA blends—primarily due to the inclusion of PHA. Investigating the effect of soil amendments—HWDR, HWDR+PJ, LWDR and LWDR+PJ—in Study 2 revealed that LWDR and HWDR played an equally effective role in decreasing the tensile strength and M_n of MB-PLA+PHA blends. Study 3 compared MB-PLA+PHA blends to starch based commercially available “biodegradable” film “BioTelo. MB mulches, including PLA/PHA blends underwent a greater percent loss of physico-chemical properties than BioTelo (e.g., tensile strength and M_n). MB-PLA+PHA-75/25 in Study 4 elucidated that the degradation was primarily due to microorganisms rather than abiotic factor (e.g., moisture) –determined from the greater loss of tensile strength for mulch in nonsterilized soil rather than sterilized soil. Additionally, the greater decrease of M_n of mulch in nonsterilized soil (14%) compared to sterilized soil (9%) supports the role of microorganisms in the degradation of MB-PLA+PHA-75/25. The importance of soil temperature, simulating cool,warm, and moderate environment, on the biodegradation of MB-PLA+PHA blends was evaluated in Study 5. At the low soil temperature, 15°C, the loss of tensile strength and M_n of MB-PLA+PHA-75/25 was relatively lower than at 20 or 23^{o}C. The addition of PHA into the MB PLA feedstock led to reduction of the reaction order for PLA based nonwoven mulches; for instance, the rate changed from first to zeroth order for tensile strength and M_n in MB-PLA+PHA-75/25. Chapter 8 involved the study examining the effect of simulated weathering on physico-chemical parameters and the inherent biodegradability under composting conditions for several nonwoven mulches, including MB-PLA+PHA-75/25. The decrease of physico-chemical properties such as 95% of tensile strength and 32% of M_n, in addition to decrease of T_g from 65 to 57^{o}C for MB-PLA+PHA-75/25 elucidates the effect of important abiotic factor, sunlight. After simulated weathering, MB-PLA (93%) and MB-PLA+PHA (91%) underwent a similar extent of biodegradation; however, the rate of biodegradation for MB-PLA+PHA blends was higher than MB-PLA. MB-PLA+PHA can potentially serve as a "Class II" (environmental degradation of materials by simulated weathering prior to soil burial) material that complies with ASTM WK 29802 (standard specification for biodegradability of agricultural plastics in soil). Subsequently, it may satisfy the National Standard Organic Board (NOSB) criteria— 90% biodegradation in two years, completely biobased and contains no prohibited feedstock. Thus, MB-PLA+PHA and to lesser extent, MB-PLA can be regarded as a mulch materials to be used in US organic fields as required by NOSB.

9.1.4 UNDERLYING MECHANISM FOR BIODEGRADATION OF MELTBLOWN (MB) MULCHES (PLA AND PLA/PHA BLENDS)

A hypothesis for the different stages of biodegradation and the change of physico-chemical parameters during the stage, explained in Section 2.5.3 and displayed in Fig.10, was examined in this dissertation for MB nonwoven agricultural mulches via soil burial tests and simulated weathering, followed by testing of inherent biodegradability under composting conditions (ASTM D5338). The biodegradation of MB mulches employed in Studies 2-6 was determined by the loss of tensile strength and number-average molecular weight (M_n) and variations of thermal properties such as glass transition temperature (T_g), melting temperature (T_m) and melting enthalpy (ΔH_m) and enthalpy of crystallization (ΔH_c) and percent of crystallinity of PLA component (X_c). In addition, microfiber breakage was observed in scanning electron microscopy (SEM), and surface modification, due to hydrolysis, was determined via Fourier transform infrared spectroscopy (FTIR) analysis.

Tensile strength loss, analyzed in Studies 2-6, was the best measure for observing the biodegradation of PLA based MB mulches. The greatest loss of tensile strength in 10 wk—85-94% in Studies 2,3,5 and 6 validated the first stage of biodegradation (i.e., >50% of loss of tensile strength). [Tensile strength testing was not performed after 30 wk of soil burial study for MB mulches because of extreme fragmentation]. In addition, the loss of M_n for MB mulches was > 20% during 30 wk of soil burial (Studies 2, 3, 5 and 6),—a strong support to the hypothesis, as illustrated in Fig.10. The Fox-Flory Equation (Eqn.3) given in Chapter 3 demonstrates, the loss of M_n is proportional to a decrease of T_g. The results of Study 4, which differentiated abiotic hydrolysis from microbial degradation, suggested that PLA underwent biodegradation rather than two-step process involving chemical hydrolysis, followed by microbial assimilation of polymers, in contrast to the underlying mechanism of the first stage of biodegradation as depicted in Fig. 10 . Particularly, the importance of microorganisms in the first stage of biodegradation was evidenced by a greater loss of tensile strength in nonsterilized soil compared to sterilized soil. Therefore, the results of Study 4 demonstrate the role of microorganisms in mulch biodegradation for the soil burial studies in this dissertation as well (Study 2, 3, 5 and 6). Microfiber breakage, observed via SEM analysis in Study 2, supported the hypothesis that partial mineralization occurred in 30 wk soil burial studies, during the first stage of biodegradation.

The effect of several important environmental factors on biodegradation was examined in this dissertation. A soil amendment, pineapple juice, was employed as an additional carbon-energy source to microorganisms in Study 2 to enhance the biodegradation of PLA based nonwoven mulches. However, the physico-chemical properties (e.g., tensile strength, and M_n) were not affected significantly. in contrast to, equally effective low and high water delivery rates [LWDR and HWDR]. The water delivery rates (LWDR and HWDR), that maintained soil moisture at the optimal level (33-37%), decreased the M_n and tensile strength of the MB mulches significantly. Study

5 assessed an important parameter in the biodegradation of PLA based mulches, soil temperature. Soil temperatures that occur in spring- and winter-like environments, simulated by employing a soil temperature of 15^{o}C, did not affect the PLA based mulches (thermal properties, particularly $\Delta H_{c,}$ and T_g and depolymerization via GPC and FTIR analysis) due to low soil microbial activity. However, summer like environment, simulated by soil temperature (23^{o}C), and ambient soil temperature (20^{o}C) influenced the biodegradation (tensile strength, depolymerization, and thermal properties, particularly ΔH_m) to a similar extent. Nevertheless, Study 5 suggested that biodegradation (depolymerization and thermal properties, particularly X_c, and T_g) at low soil temperature (15^{o}C) was relatively lesser than 20 and 23^{o}C.

FTIR analysis, performed in Studies 2 and 5, confirmed that depolymerization occurred via ester bond hydrolysis [corresponding to a decrease in the –C=O stretching spectral band at 1740-1751 cm^{-1} and increase of the –OH stretching region at 3100-3500 cm^{-1}]. However, there was no new bond formation at 1585 and 1718 cm^{-1} pertaining to –C=C— bonds and free carboxylic acid groups, respectively, suggesting the absence of UV light penetration on the top layer of soil.

Study 6 examined the kinetics of biodegradation for MB-PLA and MB-PLA+PHA. The biodegradation of MB-PLA+PHA blends followed zeroth order reaction rate for the loss of tensile strength and M_n, whereas MB-PLA followed zeroth order for the loss of M_n and second order for the loss of tensile strength. Thus, the inclusion of PHA in the PLA based mulch improved the biodegradation. Previous studies reported that PLA underwent first-order degradation during hydrolysis, determined from the loss of tensile strength and $M_{n.}$

9.2 SIMULATED WEATHERING

Simulated weathering, was conducted for PLA based MB mulches. Results suggested that weathering of mulches increased the rate and extent of hydrolysis of MB-PLA and MB-PLA+PHA-75/25, observed from the loss of tensile strength, M_n and thermal properties, particularly ΔH_m and T_g. In addition, weathered MB-PLA+PHA-75/25 underwent greatest rate of biodegradation, measured via ASTM D5338 (biodegradability under composting conditions). Therefore, when evaluating the biodegradability of plastic mulches, the effect of weathering and environmentally related factors on the rate and extent of biodegradation is important.

9.3 RECOMMENDATIONS

9.3.1 SOIL BURIAL STUDIES

When conducting soil burial study, the following changes in procedure are recommended. The amount of compost can be increased during the soil burial study by adding in the middle of experiment i.e., after 10 or 15 weeks, which may increase the microorganisms in the soil. The duration of soil burial study should be extended, provided experimental space is available. A soil burial study can also be conducted at 35^{o}C at high moisture conditions to enhance biodegradation of PLA. Low water delivery rate with increased frequency, for example 500 mL of water per 24 hr, instead of high water delivery rate (1000 mL of water per 48 hr) can be provided—prevent the drainage of soil from the drainage holes of trays, and perhaps help housekeeping.

9.3.2 SOIL AMENDMENTS

Wood ash can be provided as a soil amendment in limited quantity that serve as a source of potash and maintain soil pH, which in turn increase the microbial abundance. Biochar, a good carbon source, can be used as soil amendment and determine the mulch degradation. Alternately, liquid molasses, or dry molasses possesses readily available carbon and can be employed as a soil amendments to enhance the biodegradation of mulches. Mushroom compost is also a possible soil amendment to test the biodegradation of mulches.

In all these suggested amendments, quantification of soil microorganisms is required to ensure enhanced microbial degradation.

9.3.3 SIMULATED WEATHERING AND ASTM D5988

SB nonwoven are recommended for long-term agricultural applications such as row covers. MB nonwoven, particularly MB-PLA+PHA blends, are recommended as “Class II” material in ASTM WK 29802. In order to mimic the real agricultural field conditions, after simulated weathering, the biodegradability at ambient conditions—ASTM D5988—should be performed. Intermittent addition of compost is also required if ASTM D5988 is performed.

9.3.4 NONWOVEN PREPARATION

Nonwoven consisting of PLA+ PHA- 90/10 can also be prepared and tested in soil burial studies because 90% of PLA in the polymer blends would provide stiffness i.e., a slight increase in tensile strength. If fillers are used in the nonwovens processing, it can be either starch or cellulose—to increase microbial abundance after soil burial as starch and cellulose undergo biodegradation in any form. Other possibility to increase the microbial degradation of PLA is to prepare nonwoven—MB or SB—mulches with low molecular weight, ($M_n \leq 50{,}000$ kDa), and low melting temperature (T_m) feedstock. Low weight (grams per square meter) nonwoven mulches can also prepared and subjected to soil burial test and /or simulated weathering.

9.3.5 ADDITIONAL ANALYSES OF RETRIEVED NONWOVEN MULCHES

X-ray diffraction experiment can be conducted to confirm the crystallinity obtained from differential scanning calorimetry (DSC). After conducting ASTM D5338 or 5988 or soil burial studies, gel permeation chromatography on the debris remaining in the bioreactor can be performed to understand the degradation mechanism (bulk or surface erosion). In order to understand the cross-link density of polymers, gel content should be determined.

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