



Performance and Adoptability **Biodegradable Mulch**

biodegradablenmulch.org

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Summary

The methods to assess and quantify deterioration and biodegradation of biodegradable plastic mulches are explained here. The USDA Specialty Crops Research project, Performance and Adoptability of Biodegradable Mulch for Sustainable Specialty Crop Production, is using these methods to develop an understanding of the causes and mechanisms of biodegradation and to assess the performance of biodegradable plastic mulches.

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Finding Out How Biodegradable Plastic Mulches Change Over Time

INTRODUCTION

Biodegradable plastic mulches (BDMs) are thin plastic films that farmers use in growing fruits and vegetables. BDMs serve as a physical barrier to prevent weeds and loss of soil moisture due to evaporation. After the fruits and vegetables are harvested, the mulches (which are partially broken down due to sunlight, rain, and wind) are tilled into the soil, where they are biodegraded by soil microbes, which convert the plastic's molecules into carbon dioxide (CO₂) and water.

ANALYSIS OF MULCH DETERIORATION DURING STORAGE AND USE IN THE FIELD

Analysis of BDMs' properties (physical and chemical) is useful to monitor deterioration throughout their life cycle, particularly at three different life stages of the BDMs:

1. During long-term storage of BDMs;
2. During its use in the field (to measure deterioration due to environmental factors); and
3. During BDM biodegradation process after the BDMs' utility stage is complete.

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An agricultural producer lays a biodegradable plastic mulch film before planting.

(Photo: Randy Honcoop)

The first assessment is needed to ensure the structural integrity of the BDMs during long-term storage. To prevent deterioration, BDMs should be stored indoors at ~22°C, at low relative humidity, and covered with dark colored plastic bags to prevent exposure to light. The second assessment is to determine whether and how sunlight, wind, rain, and/or other events occurring in the field promote deterioration of the BDMs, since field breakdown can have a direct impact on the biodegradation process. The third assessment is important to better understand the underlying events that occur during BDMs' biodegradation in the soil or under composting conditions.

Common physical, visual, and chemical analyses of BDM deterioration are listed in Table 1 (see following page). To assess deterioration during storage or field use, physical and visual methods will be the most relevant. Physical tests quantify the extent of change in the mechanical strength of the BDMs using standardized tests. Tensile strength (a measurement of the force required to break the BDMs when pulled from both ends) and percent elongation at failure (increase in length of BDM after it is pulled to its maximum amount) are the most useful physical measurements, providing direct and quantifiable data that reflect the weakening and embrittlement of the mulch. The two are measured using specialized tensile strength testers, which are governed using standardized testing procedures. For the two measurements, it is important that the BDM samples used for the test be structurally intact (without holes or tears), and free of soil particles. A procedure has been developed for cleaning BDM samples through careful brushing with a soft bristle brush. It is important that the samples be carefully cut into rectangular pieces, with the lengthwise direction of the samples oriented with the "machine direction" of the BDMs, referring to the direction the BDM rolls are produced and laid in the field.



Before being subjected to the tensile strength assessment, the biodegradable plastic mulch samples retrieved from the field test site are cleaned through careful brushing with a soft bristle brush.

ANALYSIS OF MULCH DETERIORATION DURING BIODEGRADATION IN THE SOIL

Monitoring of biodegradation under controlled laboratory settings and in the field requires different types of analyses. Laboratory experiments are used to better understand the biodegradation process and the impact of specific environmental parameters or variables such as BDM chemical composition or thickness. The laboratory experiments are frequently conducted in closed vessels under controlled conditions (e.g., temperature or soil moisture). Such a configuration enables biodegradation to be directly measured through quantifying the release of CO₂, using a gas sensor or chemical titration method. CO₂ is one of the final breakdown products when microbes 'digest' the BDMs.

Because measuring CO₂ production in the field is not practical, other methods to assess degradation are needed. Visual assessments are a primary means of monitoring deterioration outside of a laboratory. Several of the physical and visual approaches listed in Table 1, such as the loss of tensile strength and/or % elongation, are also useful assessments for field-based studies, if testing facilities and expertise are available. In addition, weight loss (decrease of mass per unit area), decrease of thickness, and decrease of area (by analyzing digital photographs of BDM fragments) can be used for the same purpose, if the BDM samples are thoroughly and carefully cleaned. The disappearance of

Table 1. Physicochemical analyses employed to evaluate degradation and deterioration of BDMs during the three BDM life stages.

Analysis	BDM Life Stages *	Comments
A. Physical / Mechanical		
Tensile Strength; elongation at failure	1-3	Detects physical strength and brittleness
Weight loss	3	Mulches must be cleaned of soil
Thickness	3	Several different standardized methods can be used
B. Visual		
Photography	1-3	The same BDM sample is photographed over time, using comparable photographic conditions
Colorimetry	1,2	Detects the bleaching of colored pigments due to sunlight
Macroscopic deterioration	2	Percent visual deterioration (PVD) or percent soil exposure (PSE) are quantified in 5% increments from 0% (completely intact) to 100% (completely deteriorated)
Decrease of area	3	BDM fragments are collected and then photographed; area is determined through imaging software after the photograph is digitized
Scanning electron and laser confocal microscopies	1-3	Detection of degradation on the microscopic level; detection of adsorbed soil and microorganisms
C. Chemical		
Fourier Transform Infrared (FTIR) Spectrometry	1-3	Changes in chemical bonding, due to photochemical reactions, hydrolysis of ester bonds, etc.
Molecular weight analysis	3	Gel permeation chromatography (GPC), viscometry, mass spectroscopy; measures depolymerization
Thermal properties	1-3	Differential scanning calorimetry (DSC); quantifies depolymerization and changes in crystallinity; requires knowledge of polymeric constituents
Nuclear magnetic resonance (NMR)	1-3	Detects changes in relative amounts of biopolymeric constituents; requires knowledge of constituents
Ash content (or elemental or thermogravimetric analysis)	1-3	Detects relative amounts of inorganic and organic constituents
Radiocarbon analysis	3	Detects relative difference in polymeric constituents due to differences in their carbon isotope profile

* 1 = long-term storage; 2 = use in the field (e.g., weathering); and 3 = after use is complete.



A research assistant affixes the biodegradable mulch sample to the clasps of the tensile strength analyzer. The tests are governed by standardized testing procedures.

polymeric constituents from BDMs can be monitored through elemental analysis and measuring ash content. The latter measurement involves subjecting the BDM to a high temperature, so that the BDM's polymeric and organic constituents are removed, and what remains are inorganic molecules such as salts. The loss of mass during the high temperature treatment is used to assess the amount of polymeric and other organic constituents through a mass balance calculation.

Changes in physical and chemical properties of the BDMs serve as complementary information to CO₂ production data and visual assessments, providing a deeper understanding of the biodegradation process. For instance, previous research (Dharmalingam et al., 2016) suggests that the biodegradation process involves two major stages: an initial stage during which the structure of BDMs is “opened up” (observed by a decrease of

tensile strength) concurrent with colonization by microbes in the vicinity of the BDMs, followed by a slow and steady ‘using up’ of the plastic by microorganisms (second stage).

The second stage of biodegradation is best studied using chemical analyses of the BDMs, particularly when the BDMs' chemical composition is known. The simplest and most universal chemical test is to determine the decrease in average molecular weight of the polymers (“depolymerization”). Molecular weight, which relates to the length of the molecular chains, decreases steadily during the second stage. This change reflects the activity of microorganisms at the ends of the polymer chains. Gel permeation chromatography (GPC) is the most commonly used approach to determine molecular weight. Another common approach is to measure intrinsic viscosity, a measure of the polymer's contribution to the viscosity of a polymer-organic solvent solution, which is determined by comparing viscosity measurements at several different polymer concentrations. The intrinsic viscosity is directly related to the molecular weight through a power-law relationship known as the Mark-Houwink equation. However, a limitation of GPC and viscosity is that the analyses apply only to BDM components that dissolve in the solvent (e.g., chloroform or tetrahydrofuran). Fortunately, many of the polyesters commonly encountered in BDMs, such as polybutylene adipate terephthalate (PBAT), polylactic acid (PLA), and polyhydroxybutyrate (PHB) dissolve in commonly used solvents; however, other common BDM constituents such as starches do not.

Other methods that measure changes in chemical properties of BDMs during biodegradation require prior knowledge of the composition of the BDMs. Thermal properties of polymers are measured via differential scanning calorimetry (DSC), a method that measures the difference in the amount of heat required to increase the temperature of a BDM relative to the heat required to increase a reference material to the same temperature, at several different temperatures. The resultant DSC “thermogram” (heat vs. temperature) provides information on phase transitions for polymers, enabling calculation of the amount of crystallinity, for instance. Crystallinity is important for understanding the first stage of biodegradation, since microbes preferably utilize regions of lower crystallinity as carbon sources during their establishment. Changes in relative amounts of polymeric constituents during biodegradation are monitored via FTIR, nuclear magnetic resonance (NMR) spectroscopy and radiocarbon analysis. NMR is a common chemistry spectroscopic method that

provides molecular structure of organic substances. Radiocarbon analysis can be used to identify and quantify different polymers through measurement of a BDM's carbon isotope profile (ratio of carbon atoms possessing specific atomic weights: ^{12}C , ^{13}C , and ^{14}C).

CONCLUSIONS

Measurements of physical (mechanical), visual and chemical properties of BDMs during their storage, deployment in the field, and biodegradation in the soil can be carried out using the “toolbox” of methods listed in Table 1. These methods provide a means to assess and quantify deterioration and biodegradation for both field and laboratory settings, and to more deeply understand the underlying causes and mechanisms of biodegradation. A goal of our USDA Specialty Crops Research project, *Performance and Adoptability of Biodegradable Mulch for Sustainable Specialty Crop Production*, is to further develop the methodologies and apply them to a diverse set of BDMs and environmental conditions in both the field and the laboratory.

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