Report on Biodegradable Biobased Mulch Films

This report describes the biobased and non-biobased content of the current commercially available biodegradable biobased mulch films (BBMFs). It also describes in further detail the definition of "biobased" as referenced in the USDA organic regulations, and the factors that manufacturers consider when formulating BBMFs for the current market.

Background

Biodegradable mulch films made from bioplastics were first petitioned in 2012[1] by the Biodegradable Products Institute (BPI; S. Mojo 2012) for addition to the National List as an allowed synthetic for crop production. The petition suggested that mulch films should be defined by the following criteria:

(1) *Meets the requirements of ASTM Standard D6400 or D6868 specifications, or of other international standard specifications with essentially identical criteria, i.e. EN 13432, EN 14995, ISO 17088; and*
(2) *Shows at least 90% biodegradation absolute or relative to microcrystalline cellulose in less than two years, in soil, tested according to ISO 17556 or ASTM D5988.*

The petition did not suggest a standard for measuring biobased content. However, after considering the petition, the National Organic Standards Board (NOSB) Crops Subcommittee published a proposal in August 2012 to list these materials on §205.601(b)(2) :

> *Mulches: (iii) Biodegradable biobased bioplastic mulch meeting the following criteria: (A) Completely biodegradable as shown by: 1) meeting the requirements of ASTM Standard D6400 or D6868 specifications, or of other international standard specifications with essentially identical criteria, i.e. EN 13432, EN 14995, ISO 17088; and 2) showing at least 90% biodegradation absolute or relative to microcrystalline cellulose in less than two years, in soil, tested according to ISO 17556 or ASTM D5988; (B) Biobased certified using the ASTM D6866 method; (C) Must be produced without excluded methods; (D) Must be produced without engineered nanomaterials; and (E) Grower must take appropriate actions to ensure complete degradation at the end of each growing or harvest season.*

The full NOSB later recommended the subcommittee proposal, after removing the exclusion of engineered nanomaterials[2] (NOSB 2012), and adding the requirement that the mulch films be "biobased" certified using the ASTM D6866 method. The full NOSB recommendation also proposed a new definition in 205.2 for biobased: "organic material in which carbon is derived from a renewable resource via biological processes. Biobased materials include all plant and animal mass derived from carbon dioxide recently fixed via photosynthesis, per definition of a renewable resource (ASTM)." The NOSB recommendation goes on to explain the requirement, stating "a good definition of 'biobased material' [has been provided by the board] to ensure that this testing protocol is meaningful." The board explained its intent to define biobased so "that this category would not allow products, for example those made from aliphatic aromatic copolymers (AACs), which come from petroleum" (NOSB 2012). In 2014 the NOP

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[1] The original petition called them "Biodegradable Mulch Film made from Bioplastics" (S. Mojo 2012)
[2] The NOSB removed this requirement due to the lack of an officially recognized definition of nanomaterials.

published the final rule (FR Vol.79, No. 189), allowing with restrictions any BBMF that meets the following definition in 205.2:

> *(1) Meets the compostability specifications of one of the following standards: ASTM D6400, ASTM D6868, EN 13432, EN 14995, or ISO 17088 (all incorporated by reference; see Sec. 205.3); (2) Demonstrates at least 90% biodegradation absolute or relative to microcrystalline cellulose in less than two years, in soil, according to one of the following test methods: ISO 17556 or ASTM D5988 (both incorporated by reference; see Sec. 205.3); and (3) Must be biobased with content determined using ASTM D6866*

The final rule also indicated in the BBMF listing in 205.601 that these mulches must be produced without organisms or feedstock derived from excluded methods.

After publication of the final rule, there was confusion among Material Review Organizations (MROs) and certification agencies about how much of the feedstocks must be biobased. The current market of BBMFs appears to have only a small portion of biobased feedstocks, with the remaining being derived from petroleum sources. In response, the NOP published Policy Memo 15-1 (2015), which clarified that all BBMF feedstocks must be biobased, and that synthetic polymer feedstocks, such as petrochemical resins, do not comply with the USDA organic regulations. As such, it is understood by the organic industry that there are no BBMFs on the market that meet this requirement at the time of this report although they are compliant with the requirements for compostability and biodegradability, according to the appropriate ASTM standards.

Biobased Definitions

There are several definitions pertinent to the discussion of BBMFs. First, the ASTM definition for “biobased material” is “organic material in which carbon is derived from a renewable resource via biological processes. Biobased materials include all plant and animal mass derived from CO_2 recently fixed via photosynthesis, per definition of a renewable resource.” This definition was adopted by the NOSB in their formal recommendation, but was not carried over into the final rule. ASTM D6866 testing measures the biobased content in materials, and results are reported as a percentage. For example, the test for a mulch film would yield a percentage between 0-100%, and this percent would be its “biobased content.” The biobased content is determined by detecting the level of carbon-14 (^{14}C), which is found in biobased materials but not in fossil fuels (Niaounakis 2013).

ASTM D6852[3] (2011) further defined a biobased <u>product</u> as a “product generated by blending or assembling of biobased materials, either exclusively or in combination with non-biobased materials, in which the biobased material is present as a quantifiable portion of the total mass of the product. Biobased material in a multicomponent product should be measured on a component basis rather than on the whole product.” However, this standard was withdrawn in 2011 and no official final version was published. The USDA also defines biobased products as “commercial or industrial products that are composed in whole, or in significant part, of biological products or renewable domestic agricultural materials or forestry materials” (USDA 2015). The USDA oversees the BioPreferred® Program, which verifies several

[3] ASTM D6852: Standard Guide for Determination of Biobased Content, Resources Consumption, and Environmental Profile of Materials and Products

categories of products with biobased content. The program uses minimum standards for biobased content for different categories, and products must meet these standards in order to use the program's seal.

Contents of Commercially Available Biodegradable Biobased Mulch Films

There are several commercially available brand name mulch films that are biodegradable, and that also contain some portion of biobased content as measured by ASTM D6866. For the purposes of this report, and to protect proprietary information, generalizations will be made about different types of feedstocks used to make the mulches, including the biobased and non-biobased materials, and no brand names will be disclosed. Information for this portion of the report was derived from interviews with various mulch and raw material manufacturers (see References). It should be noted that most BBMFs contain dyes or tints (to lend the desirable film color), but since these are not resin feedstocks, they will not be discussed in any detail.

In general, BBMFs are composed of some portion of a biobased polymer in combination with a petroleum derived polymer. Typically, the films are produced by the manufacturer (the "converter") with resin feedstocks purchased from "raw material suppliers." It is important to note that the mulch films are usually made from one resin, and are not further blended by the converter with other materials besides processing aids or dyes. Therefore, the biobased content appears to be controlled by the raw material suppliers and the discussion on biobased content centers mainly on the raw resin material itself. As indicated by Yepson, et al. (2015), since the raw material resin is the only feedstock that forms the final mulch film, the resin should be tested and assessed for biobased content, rather than the final mulch film.

<u>Biobased Materials and Content of Resins</u>

There are currently two main suppliers of raw materials for making BBMFs for the U.S. market. A few additional raw material suppliers exist but they do not have any of the market share at the time of this report. One of the main raw material suppliers uses polylactic acid (PLA) as the main biobased material in their biodegradable resin feedstock. The basic building block of PLA is lactic acid, which is converted to high molecular weight PLA through various complex chemical pathways, such as condensation/coupling, azeotropic dehydrative condensation, or ring-opening polymerization of lactide (Garlotta 2002). According to Natureworks, LLC (2015), the vast majority of PLA produced globally today is produced in the U.S. and currently uses lactic acid produced by genetically modified yeast (via fermentation) from a mix of non-genetically modified and genetically modified corn. One manufacturer using a small percent of PLA claims it is sourced from non-GMO starch. The biobased content for this commercially available resin is less than 10%, with the other portions being from polybutyrate adipate terephthalate (PBAT) and inorganic minerals (as processing aids). See below for more details about PBAT.

Another raw material supplier uses non-GMO starch as the main biobased component of the resin, which is coextruded with synthetic aliphatic aromatic copolyesters (S. Mojo 2012, Yepson, et al. 2015). In this process, the starch is destructured by heating and mixing with plasticizers and with other polymers (both biobased and non-biobased) that are suitable for forming BBMFs (Bastioli, et al. 1996). The other polymers in this starch based resin are polyesters that are formed from reacting an acid functional group ("diacids") with an alcohol functional group ("diols"). Monomors can be "diacids", "diols", and "bifunctional", some of which are derived from plant materials and some of which are derived from petroleum products (S. Mojo 2012, Yepson, et al. 2015). The biobased content for this commercially available resin is ~20%. See below for more information about the non-biobased polymers in the starch-based mulch film.

In summary, the biobased content for commercially available BBMFs at the time of this report ranges from ~10-20%, with the remaining portion being derived from fossil fuels or other inorganic materials such as minerals and dyes.

Non-Biobased Materials

In the currently available mulch films, the non-biobased material consists of either PBAT or various monomer components that are reacted together to form polymers. PBAT is an aliphatic aromatic copolyester produced from petroleum sources, and is considered to be fully biodegradable according to specific ASTM standards (Witt, et al. 2001). Figure 1 shows PBAT's chemical structure.

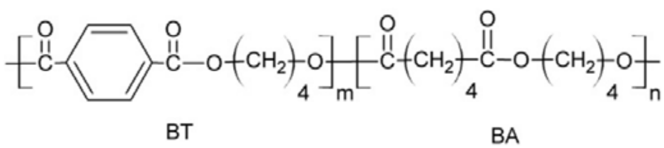

Figure 1: Chemical structure of polybutylene adipate-co-terephthalate (PBAT) **(Kijchavengkul, et al. 2010)**.

The other raw material supplier builds biodegradable polymers using various monomers from both biobased and non-biobased materials. For example, adipic acid (CAS # 124-04-9) is produced by oxidizing cyclohexane (a petroleum monomer), while sebacic acid (CAS # 111-20-6; a biobased monomer) is created by heating castor oil with sodium hydroxide. These acids may be reacted with "diol" chemicals such as 1,4-Butanediol (a petroleum product) to form polymers (S. Mojo 2012;Yepson, et al. 2015)). Table 2 below details all the known monomers (and their origin) that make up the polymers that are blended with the destructured starch to form the final raw material resin (S. Mojo 2012).

Table 1: Monomers used to make polymers in BBMFs (adapted from S. Mojo 2012)

Monomer	**CAS #**	**Source**
Lactic acid (L-, D-, DL-)	50-21-5	Fermentation from glucose by microorganisms
3-hydroxy- butyric acid	300-85-6	Created within the cell of the fermenting microorganism and converted directly into a storage carbohydrate with plastic properties
3-hydroxy-valeric acid	10237-77-1	
Adipic acid	124-04-9	Oxidation of cyclohexane
Azelaic acid	123-99-9	Oxidation of ricinoleic acid
Sebacic acid	111-20-6	Heating castor oil with sodium hydroxide
Terephthalic acid	100-21-0	Oxidation of *p*-methylacetophenone
1,4-Butanediol	110-63-4	Acetylene and formaldehyde react to form 1,4-butynediol, which is then hydrogenated
1,3-propylene glycol	504-63-2	Hydration of acrolein or fermentation of corn syrup
1,6-hexanediol	629-11-8	Hydrogenation of adipic acid

Figure 2 shows the typical pathway for BBMF manufacturing, from raw material supplier to final mulch film.

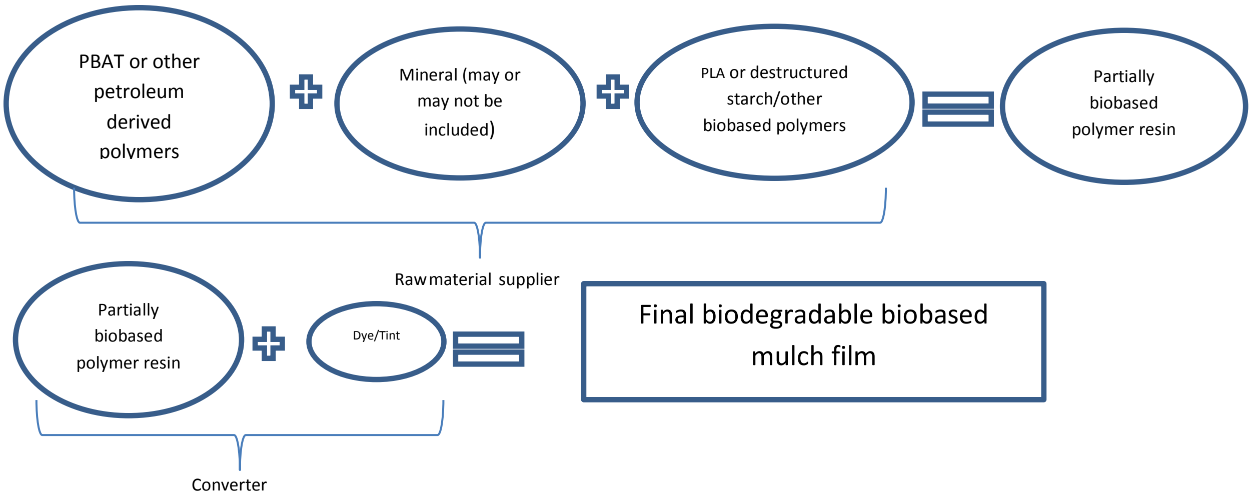

Figure 2: Commercial formulations and manufacture of currently available BBMFs (not to scale).

Factors for Formulating Biodegradable Biobased Mulch Films

According to the raw material suppliers interviewed for this report, there are several market and performance factors that contribute to the range of biobased materials present in BBMFs. While there are a variety of biobased materials on the market, only a small subset of them are also biodegradable and applicable to making BBMFs. For example, biopolyethylene (a sugar cane fermentation product) is 100% biobased but not biodegradable. Also, altering the biobased content of BBMFs would inevitably change the performance of the mulches in the field and on equipment, both of which must be thoroughly tested and significant investment must be made to accommodate the change. For example, adding more PLA to a formula increases the brittleness of the film, making it more difficult to handle and lay down (Watts 2015). The raw material manufacturers agree that all of these factors indicate that while increasing the biobased content of the BBMFs is a possibility, it will take significant financial resources and time, both of which may be barriers to eventual compliance of BBMFs for the organic sector.

References

ASTM International. "Standard Guide for Determination of Biobased Content, Resources Consumption, and Environmental Profile of Materials and Products (withdrawn 2011)." *ASTM D6852-02*. 2011.

Bastioli, C., R. Lombi, G.D. Tredici, and I. Guanella. Biodegradable compositions and films or moulded articles obtained therefrom . U.S. Patent US 5569692 A. October 29, 1996.

Garlotta, D. "A literature review of Poly (Lactic Acid)." *Journal of Polymers and the Environment* 9 (2002).

ICF International . *Biodegradable Mulch Film Made from Bioplastics.* Technical Evaluation Report, Washington D.C.: National Organic Program, 2012.

Kijchavengkul, T., R. Auras, M. Rubino, S. Selke, M. Ngouajio, and R. T. Fernandez. "Biodegradation and hydrolysis rate of aliphatic aromatic polyester." *Polymer Degradation and Stability* 95 (2010): 2641-2647.

McDonald, Stuart, interview by Lindsay Fernandez-Salvador. *Managing Director, Organix Solutions, Inc.* (May 14, 2015).

Menard, E., interview by Lindsay Fernandez-Salvador. *DuBois Agrinovation* (May 18, 2015).

Mojo, S. "Petitioned Substances Database: Biodegradable Mulch Film made from Bioplastic." *National Organic Program.* March 23, 2012. http://www.ams.usda.gov/AMSv1.0/getfile?dDocName=STELPRDC5097203 (accessed 05 14, 2015).

Mojo, Steve, interview by Lindsay Fernandez-Salvador. *Executive Director, Biodegradable Products Institute* (May 07, 2015).

Moro, M., and S. Dudek, interview by Lindsay Fernandez-Salvador. *Kaneka Americas Holding, Inc.* (May 4, 2015).

National Organic Program. *Federal Register Volume 79, Number 189.* Washington DC, September 30, 2014.

National Organic Program. *Policy Memorandum: Biodegradable Biobased Mulch Film.* Washington DC, January 22, 2015.

National Organic Standards Board . *Formal Recommendation: Biodegradable biobased mulch films.* Washington DC, October 18, 2012.

National Organic Standards Board. *Crops Subcommittee Recommendation: Biodegradable Mulch Film made from Bioplastics.* Washington, DC, August 15, 2012.

NatureWorks, LLC, interview by Lindsay Fernandez-Salvador. (May 22, 2015).

Niaounakis, M. *Biopolymers reuse, recycling, and disposal.* Waltham, MA: William Andrew, 2013.

Novamont, Inc., interview by Lindsay Fernandez-Salvador. (May 18, 2015).

Pitzi, Thomas, interview by Lindsay Fernandez-Salvador. *Technical Manager, BASF* (May 05, 2015).

United States Department of Agriculture. *Biopreferred Program.* Washington, DC., 2015.

Watts, Ruth, interview by Lindsay Fernandez-Salvador. *Sales and Business Development, BASF* (May 05, 2015).

Witt, U., T. Einig, M. Yamamoto, I. Kleeberg, W.D. Deckwer, and R.J. Muller. "Biodegradation of aliphatic-aromatic copolyesters: evaluation of the final biodegradability and ecotoxicological impact of degradation intermediates." *Chemosphere* 44 (2001): 289-299.

Yepson, R., D. Martens, M. Devellis, and A. Ferlito, interview by Lindsay Fernandez-Salvador. *Novamont North America, Inc.* (May 18, 2015).