Chapter 2
Biodegradable and Biobased Plastics: An Overview

Ramani Narayan

Abstract Plastic mulch film and sheets, rods, and tubing find increasing use in agriculture. Current polyethylene plastic mulch film is not biodegradable and therefore cannot be plowed back into the soil. It may undergo fragmentation, and the small fragments are blown all over and find its way into ocean and other pristine environments. This causes irreparable harm to ecosystems and the habitats. Completely soil-biodegradable plastics or compostable plastics offer an environmentally responsible end-of-life solution for plastic mulch film and plasticulture products. Claims of biodegradability should be qualified by the disposal environment (soil or compost), 90% + biodegradability as measured by the evolved CO_2 from the microbial process using international standards for soil biodegradability and/or compostability. However, one has to be careful of misleading claims that are prevalent in the marketplace, particularly additive-based polyolefin plastics. Using biobased carbon in place of petro-fossil carbon in the products offers a reduced carbon footprint, empowers rural agrarian economy, and reduces dependence on fossil resources.

Keywords Plasticulture · Biodegradability · Compostability · Biobased carbon · Biobased plastics

Plastic mulch film is standard practice used in agriculture to control weeds, increase crop yield, and shorten time to harvest. Other plastic materials like sheets, rods, and tubing find use in agriculture like greenhouses, small tunnels, fruit and vegetable coverings, and many more applications. About 5 million tons of plastic resin is used worldwide and growing. It contributes significantly to the economic viability of farmers, providing increased harvests, less reliance on herbicides and pesticides, more efficient water conservation, reduced plant disease, and better protection of food products. However, disposal is a major issue. The polyethylene plastic mulch film is not biodegradable in the soil environment; therefore, it cannot be plowed

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back into the soil. It may undergo fragmentation, and the small fragment is blown all over and finds its way into ocean and other pristine environments.

Burning these plastic films in the fields is not an option because it contributes to serious environmental air and particulate pollution. Therefore, this practice is being phased out and many countries have strict regulatory bans on plastic film burning. Collection, cleaning, and recycling these plastics to same or other products offers an approach to managing plastic mulch film waste, and there are several companies that offer these services.

Designing for complete biodegradability in soil after its intended use as mulch film or other plasticulture products offers an environmentally responsible value proposition. Alternatively, these mulch films can be collected and composted or anaerobically digested with farm and other bio wastes. The "complete biodegradability" approach has the potential to be more economically and technically viable than recycling as there is no need to transport, clean, recycle to usable product, and finally find markets for these recycled products.

Unfortunately, "biodegradability" is a much misused term and many misleading claims abound in the marketplace. This chapter provides a fundamental understanding of "biodegradability" and explains the science behind it. International standards to measure biodegradability in several environments like composting, anaerobic digestion, and soil are presented. Learning to understand and recognize misleading claims is discussed. This chapter also introduces the concept of "biobased" and its attendant value proposition. Biobased products offer the value proposition of a reduced carbon footprint, empowered rural agrarian economy, and reduced fossil resources dependence [1, 2].

2.1 Biodegradability—The Science

Biodegradability is an end-of-life option that allows one to harness the power of microorganism present in the selected disposal environment to completely remove plastic products designed for biodegradability from the environmental compartment via the microbial food chain in a timely, safe, and efficacious manner. Terms like "oxo", "hydro", "chemo", "photo" degradable describe abiotic (nonbiological process) mechanisms of degradation. They do not constitute or represent "biodegradability"—the biological process by which microorganisms present in the disposal environment assimilate/utilize carbon substrates as food for their life processes—see Fig. 2.1.

Because it is an end-of-life option, and harnesses microorganisms present in the selected disposal environment, one must clearly identify the "disposal environment" when discussing or reporting the biodegradability of a product—for example, biodegradability in composting environment (compostable plastic), biodegradability in soil environment, biodegradability under anaerobic conditions (in anaerobic digester environment or even a landfill environment), or biodegradability in marine environment.

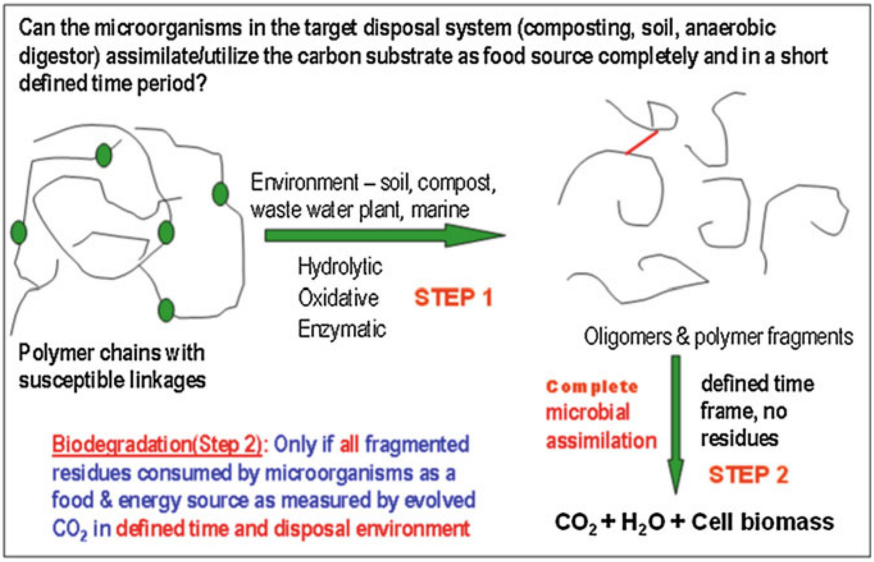

Fig. 2.1 Understanding the biodegradability process

Reporting time to complete biodegradation or more specifically, the time required for the complete microbial assimilation of the plastic in the selected disposal environment is an important requirement. Product claims stating that plastic will eventually biodegrade based on data showing an initial 10–20% biodegradability is not acceptable and very misleading especially since the percent biodegradation levels off and reaches a plateau after some initial rate and level of biodegradation. Drawing a straight line extrapolation from the initial rate and value to 100% biodegradation is scientifically untenable, and unfortunately many of the claims are based on this type of extrapolation.

2.2 Measuring and Reporting Biodegradability

Basic biology teaches how microorganisms utilize carbon substrates as food for their life processes. Carbon substrates including any biodegradable plastics have to be transported into the microbial cell. The transport is governed by several factors like molecular weight, structure, functional groups, hydrophilic-hydrophobic balance, and other special factors. Inside the cell, the carbon is biologically oxidized to CO_2 releasing energy that is harnessed by the microorganisms for its life processes. Under anaerobic conditions, $CO_2 + CH_4$ (biogas) are produced (see Fig. 2.2). Thus, a measure of the rate and amount of CO_2 or $CO_2 + CH_4$ evolved as a function of total carbon input to the process is a direct measure of the amount of carbon substrate being utilized by the microorganism (percent biodegradation).

Aerobic process

$$\text{Glucose/C-bioplastic} + 6O_2 \longrightarrow 6CO_2\uparrow + 6H_2O;\ \Delta G^{0\prime} = -686\ \text{kcal/mol}$$

Anaerobic process

$$\text{Glucose/C-bioplastic} \longrightarrow 2\ \text{lactate} \longrightarrow 3CO_2\uparrow + 3CH_4\uparrow\ \Delta G^{0\prime} = -47\ \text{kcal/mol}$$

Fig. 2.2 Basics for the microbial utilization of carbon substrates

It would seem obvious and logical from the above basic biology lesson that to make a **claim of biodegradability**, all that one needs to do is the following: Expose the test plastic substrate as the sole carbon source to microorganisms present in the target disposal environment (like composting, or soil or anaerobic digestion or marine), and measure the CO_2 (aerobic) or $CO_2 + CH_4$ (anaerobic) evolved. A measure of the evolved gas provides a direct measure of the plastics carbon being utilized by the microorganisms present in the target disposal environment (% biodegradation). ASTM, EN, and ISO test methods teach how to measure the percent biodegradability in different disposal environments based on the fundamental biochemistry described above—irrespective of what the initial degradation is—oxo, hydro, chemo—the abiotic degradation.

Thus, one can measure the rate and extent of biodegradation or microbial utilization of the test plastic material using it as the sole carbon source in a test system containing a microbial rich matrix like compost or soil, in the presence of air and under optimal temperature conditions (preferably at 58 °C—representing the thermophilic phase). Figure 2.3 shows a typical graphical output that would be obtained if one were to plot the percent carbon converted to CO_2 as a function of time in days. First, a lag phase during which the microbial population adapts to the available test C-substrate. Then, the biodegradation phase during which the adapted microbial population begins to utilize the carbon substrate for its cellular life processes, as measured by the conversion of the carbon in the test material to CO_2. Finally, the output reaches a plateau when all of the substrate is completely utilized. Linear or any other form of data extrapolation from these complex biological systems is not acceptable and is very misleading because credible scientific substantiation for the extrapolation model does not exist.

Claims of degradable, partial or extrapolated biodegradability or eventual biodegradable are not acceptable, because it has been shown that these degraded fragments absorb toxins present in the environment, concentrating them and transporting them up the food chain [4]. Therefore, complete removal from the disposal environment in a short time period of 1–2 years is essential to eliminate potentially serious human health and environmental consequences.

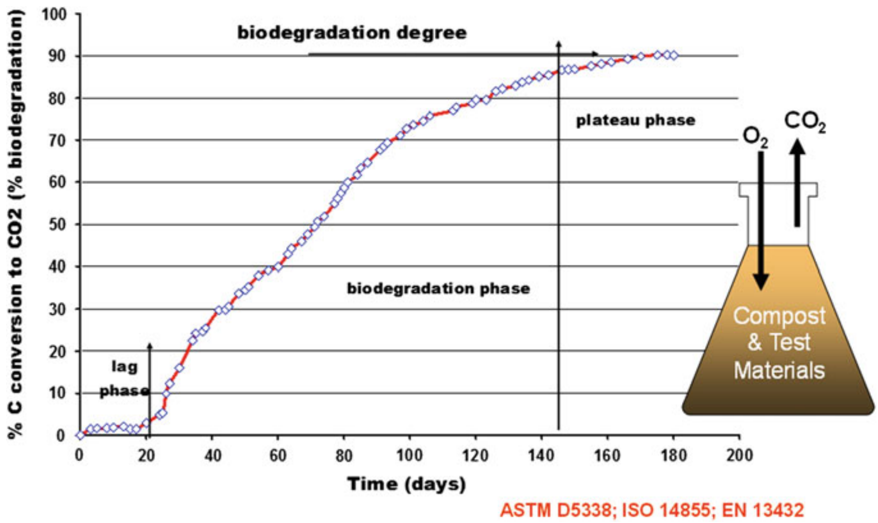

Fig. 2.3 Measuring rate and extent of biodegradability using text plastic as the sole carbon source (Reproduced with permission from [3] copyright @ 2012, American Chemical Society)

2.3 International Standards for Biodegradability

To meet the requirements of biodegradability under industrial composting conditions (compostable plastics), a plastic must satisfy the primary requirement of complete microbial utilization (biodegradability) as measured by the evolved CO_2 under composting or soil environment, as discussed in the earlier section. In addition, it has to meet the disintegration and safety criteria to claim compostability. ASTM D6400, D6868, ISO 17055, and EN 13432 are specification standards for compostable plastics. Another ISO specification standard ISO 18606 addresses "Packaging and the environment—Organic recycling" and follows the same basic principle outlined above.

Specification standards set the pass/fail criteria and is based on a standard test method. Standard test methods teach practitioners how to conduct biodegradability tests in the selected environment, how to collect data from the test, and how to correctly report the results of the tests. There are no pass/fail criteria. Unfortunately, many companies make unqualified claim of biodegradability and label their plastic product "biodegradable" referencing a standard test method without providing actual percent biodegradability values obtained in the test—a graphical display of the percent biodegradability (measured by the evolved CO_2 or $CO_2 + CH_4$) as a function of time in days. This is misleading as the consumer or stakeholder assumes that the product is completely biodegradable in a short time period. Tables 2.1 and 2.2 provide a list of international specification standards and test methods.

Table 2.1 List of international specification standards that have specified pass/fail criteria in the target disposal environment

• **Biodegradability under composting conditions—Compostable Bioplastics** • **ASTM D6400**—Specification for compostable plastics • **ASTM D6868**—Specification for plastics coatings and modifiers on paper and other compostable substrates • **ISO 17088**—Specification for compostable plastics • **EN 13432**—Specification for compostable packaging—focus on packaging • **ISO 18606**—Packaging and the Environment—Organic recycling—focus on packaging
• **Biodegradability under marine environment** • **D7021**—Specification for nonfloating biodegradable plastics in the marine environment
• **Biodegradability under soil environment** • **ASTM—**under development—90% carbon assimilation by microorganism as measured by evolved CO_2 in 2 years or less using ASTM D5988

Table 2.2 List of biodegradability test method standards from ASTM and ISO

• **ASTM D5338**—test method for measuring biodegradability under composting environment
• **ASTM D5988**—test method for measuring biodegradability in soil environment
• **ASTM D5511**—test method for measuring biodegradability in a high solids anaerobic digestor
• **ASTM D5526**—test method for measuring biodegradability in a landfill/bioreactor environment
• ***ISO 14852***—*ultimate* ***aerobic biodegradability*** *of plastic materials in an aqueous medium—Method by analysis of evolved carbon dioxide*
• ***ISO 14853***—*ultimate* ***anaerobic biodegradability*** *in an aqueous system—Method by measurement of biogas production*
• ***ISO 14855***—*Determination of the ultimate* ***aerobic biodegradability*** *of plastic materials under* ***controlled composting conditions***—*Part 1: Method by analysis of evolved carbon dioxide and Part 2: Gravimetric measurement of carbon dioxide evolved in a laboratory-scale test*
• **NOTE—**Standard test methods teach how to conduct the test and report the results. It has no pass/fail criteria and should not be used to make broad claims of biodegradability. Reporting should strictly follow the procedures laid out in the test methods showing the disposal environment, percent biodegradation, and time to achieve that biodegradation. Extrapolation of data is not permitted in these test methods

2.4 Misleading Claims of Biodegradability

There are additive-based plastics—oxo-degradable and organic additives added at 1–2% levels to conventional hydrocarbon resins like polyethylenes (PE), polypropylene (PP), polystyrene (PS), polyethylene terephthalate (PET), and other plastics that are claimed to make them "biodegradable". However, the fundamental biological data showing percent carbon utilized or assimilated by the microorganisms, as measured by the evolved CO_2 (aerobic) or $CO_2 + CH_4$ (anaerobic), are not provided. Some of the data show 10–20% biodegradation which then levels off with little or no biodegradation. Weight loss, molecular weight reductions, carbonyl index, mechanical property loss, biofilm formation, and microbial colonization do not confirm the microbial utilization of the polymeric carbon substrate, nor do they provide the amount of carbon utilized or the time to complete microbial utilization.

2.5 U.S. Federal Trade Commission (FTC) Green Guides [5]

The U.S. Federal Trade Commission (FTC) recently issued new Green Guides, on Environmental Marketing Claims to help marketers avoid deceptive environmental claims. The FTC guides state that an "unqualified degradable claim for items entering the solid waste stream should be substantiated with competent and reliable scientific evidence that the entire item will **fully decompose** (break down and return to nature; i.e., decompose into elements found in nature) **within one year** after customary disposal." It also emphasizes that unqualified degradable/biodegradable claims for items that are customarily disposed in landfills, incinerators, and recycling facilities are deceptive because these locations do not present conditions in which complete decomposition will occur within one year.

The term fully decompose into elements found in nature equates to the complete abiotic and biotic breakdown of the plastic to CO_2, water, and cell biomass via microbial metabolism. This was discussed in detail in the earlier sections.

Degradable claims can be made if it is qualified clearly and prominently to the extent necessary to avoid deception about:

- The product's or package's ability to degrade in the environment where it is customarily disposed and more importantly **the rate and extent of degradation/biodegradation**.

In the case of biodegradability claims, one has to provide "reliable and competent science based evidence" of the rate and extent of biodegradation in the target disposal environment – a graphical plot of percent biodegradability as measured by the evolved CO_2 (aerobic) or CO_2 + CH_4 (anaerobic) versus time in days. The FTC guides do not identify any specific testing protocol or specification and therefore reserve the right to evaluate the data which forms the basis of the claims. However, they clearly require that the evidence should be based on standards generally accepted in the relevant scientific fields. So ASTM, EN, ISO standards should be used to provide the evidence for validating the rate and extent of biodegradation in the selected disposal environment(s).

In summary, claims of a plastic product's biodegradability must be qualified by graphically showing the percent product carbon being utilized (percent biodegradation) by microorganisms present in the selected disposal environment as measured by the evolved CO_2 (aerobic) or CO_2 + CH_4 (anaerobic) as a function of time in days in the selected disposal environment.

2.6 Biobased Plastics

Biobased plastics are "plastics in which the (organic) carbon (of the polymer molecule) in part or whole comes from plant-biomass like agricultural crops and residues, marine and forestry materials, algae, and fungi **living in a natural environment in equilibrium with the atmosphere**". Figure 2.4 explains the fundamental concept behind biobased plastics

Note: Plastics in which the (organic) carbon comes from petroleum, natural gas, and other fossil resources are not biobased.

Plastics—Material which contains as an essential ingredient a carbon-based high polymer and which at some stages in its processing into finished product can be shaped by flow
Biobased—containing organic carbon of renewable origin like (from) agricultural, plant, animal, fungi, microorganisms, marine, or forestry materials living in a natural environment in equilibrium with the atmosphere—ASTM D6866
Organic Material(s)—material(s) containing carbon-based compound(s) in which the carbon is attached to other carbon atom(s), hydrogen, oxygen, or other elements in a chain, ring, or three dimensional structures—IUPAC nomenclature

ASTM D6866-16—Standard Test Methods for Determining the Biobased Content of Solid, Liquid, and Gaseous Samples Using Radiocarbon Analysis provide the following definitions related to biobased plastics:

Biobased—containing organic carbon of renewable origin like agricultural, plant, animal, fungi, microorganisms, marine, or forestry materials living in a natural environment in equilibrium with the atmosphere.

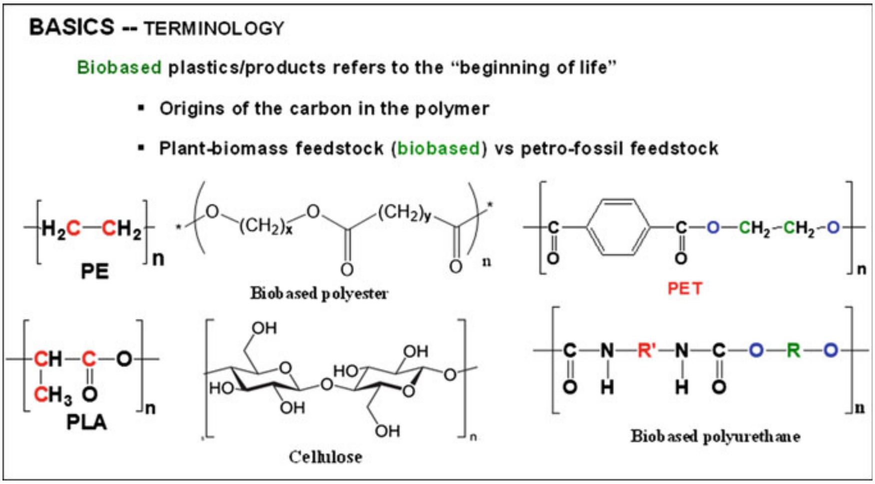

Fig. 2.4 Fundamental concepts for biobased plastics

biobased carbon content—the amount of biobased carbon in the material or product as a percent of the total organic carbon (TOC) in the product
biobased carbon content on mass basis—amount of biobased carbon in the material or product as a percent of the total mass of product
biogenic—containing carbon (organic and inorganic) of renewable origin like agricultural, plant, animal, fungi, microorganisms, macroorganisms, marine, or forestry materials
biogenic carbon content—the amount of biobased carbon in the material or product as a percent of the total carbon (TC) in the product
biogenic carbon content on mass basis—amount of biogenic carbon in the material or product as a percent of the total mass of product.

2.7 Application

USDA biopreferred program and EPA Greenhouse gas reporting requirements (D7459) use ASTM D6866 as does Japan EcoMark (http://www.ecomark.jp) program. The EU-CEN standards are in harmony with ASTM and ISO standards and use the same basic principles of radiocarbon analysis enunciated in ASTM D6866. European certification organizations are Vincotte, Belgium (OK biobased), DIN-CERTCO (Germany).

The biobased carbon value proposition for plastics does not address its end-of-life—the question of what happens to product after use when it enters the disposal environment. Biobased plastics are not necessarily biodegradable-compostable and all biodegradable-compostable plastics are not automatically biobased. The biobased carbon content has zero impact on the end-of-life of the biodegradable plastics. The molecular structure of the plastic and the availability of its carbon for transport into the microbial cell and subsequent utilization for energy drive the microbial assimilation (percent biodegradability) of carbon substrates like plastics—the availability of carbon in a molecule to the microbes and not the source of the carbon is the key learning.

Value proposition for "biobased"

Replacing petro/fossil carbon with biobased carbon (from plant-biomass feedstocks) in plastics and industrial products offers the value proposition of removing carbon present as CO_2 in the environment and incorporating it into a polymer molecule via plant-biomass photosynthesis in a short time scale of 1 (agricultural crops, algae) to 10 years (short rotation wood and tree plantations) in harmony with Nature's biological carbon cycle. Plastics made from petro/fossil resources (like Oil, Coal, Natural gas) which are formed from plant-biomass over millions of years and so cannot be credited with any CO_2 removal from the environment even over a hundred-year time scale (the time period used in measuring global warming

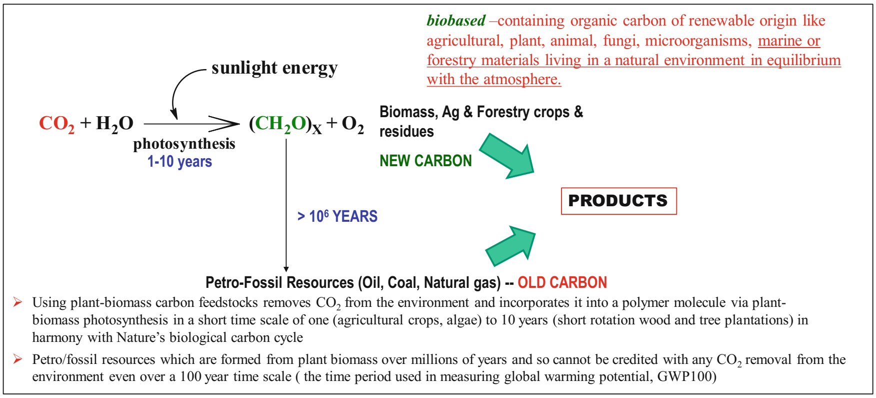

Fig. 2.7 Illustrating zero material carbon footprint using biobased carbon

potential, GWP100). Process carbon and environmental footprint (arising from the process of converting the feedstock to product) are also improved. This concept is shown in Fig. 2.5.

The biobased carbon content of products is determined independently and unequivocally using radio carbon analysis as codified in international standards—the primary one is the ASTM D6866 (Standard Test Method for determining biobased (carbon) content of solids, liquids, and gaseous samples using radiocarbon analysis). Using experimentally determined biobased carbon content and applying fundamental stoichiometric calculations, one can readily calculate the amount of CO_2 removed from the environment by 1 kg of material. For example: 1 kg of biobased polyethylene (PE) containing 100% biobased carbon content would result in removing 3.14 kg of CO_2 from the environment. 1 kg of PLA (100% biobased carbon content) would remove 1.83 kg of CO_2 from the environment. 1 kg of the current bio PET (20% biobased carbon content—only the glycol carbons come from plant-biomass) results in 0.46 kg of CO_2 removal from the environment. 1 kg of the 100% biobased carbon content PET results in 2.29 kg of CO_2 removal. In contrast, the petro-fossil carbon-based products result in zero CO_2 removal from the environment. These results are graphically shown in Fig. 2.6.

Eventually, at the end-of-life of these plastics, the carbon will be released back into the environment as CO_2 through waste-to-energy systems or incineration or through composting or anaerobic digestion (if it has biodegradability-compostability feature built into it). However, the CO_2 released will be captured by the next season's crop or biomass plantation resulting in a net zero material carbon footprint, in harmony with Nature's carbon cycle. In contrast, the non-biobased PE or PP will contribute a net 3.14 kg of CO_2 into the environment for every 1 kg of PE used. 1 kg of PET will contribute 2.29 kg of CO_2 to the environment. Figure 2.7 graphically reports these numbers and illustrates the zero carbon footprint concept.

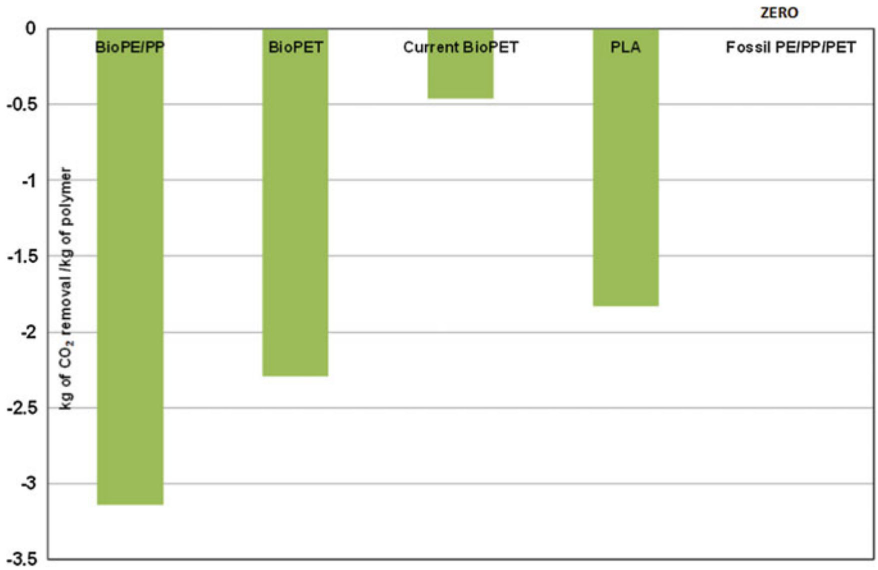

Fig. 2.6 Material carbon footprint—Amount of CO_2 removed from the environment per kg of resin

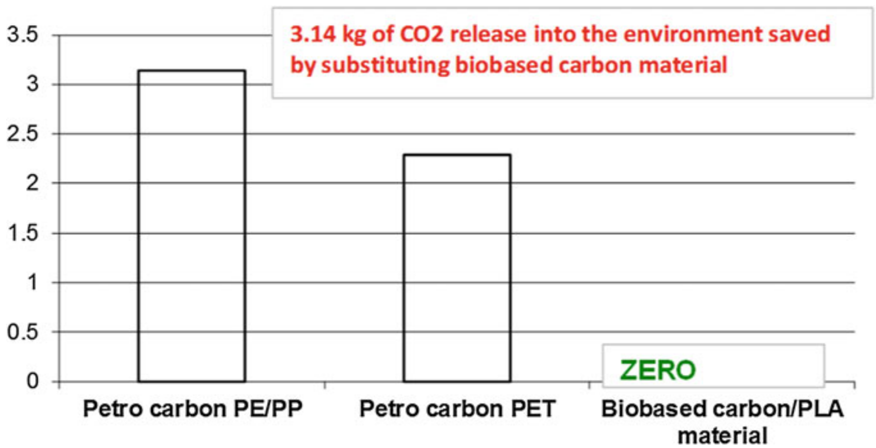

Fig. 2.5 Value Proposition for using biobased versus petro/fossil carbon—the material carbon footprint

In summary, the replacement of petro-fossil carbon in whole or part by biobased carbon (derived from plant-biomass resources) offers the value proposition of reduced carbon footprint and the enabling technology to move toward the closed loop “circular economy” model that is being advocated and adopted by many nations and major industrial organizations and brand owners.

2.8 Conclusions

Truly and completely soil-biodegradable plastics or compostable plastics offer an environmentally responsible end-of-life solution for plastic mulch film and other plasticulture products. However, one has to be careful of misleading claims that are prevalent in the marketplace, especially additive-based polyolefin plastics. International standards for soil biodegradability or compostability should be met for claims of biodegradability and the disposal environment, extent and rate of biodegradation should be clearly documented.

Using biobased carbon in place of petro-fossil carbon in the products offers a value proposition of reduced carbon footprint, empowered rural agrarian economy, and reduced fossil resource dependence.

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