Biobased material/product

Organic material/product containing in whole or part biogenic (biological sources) carbon

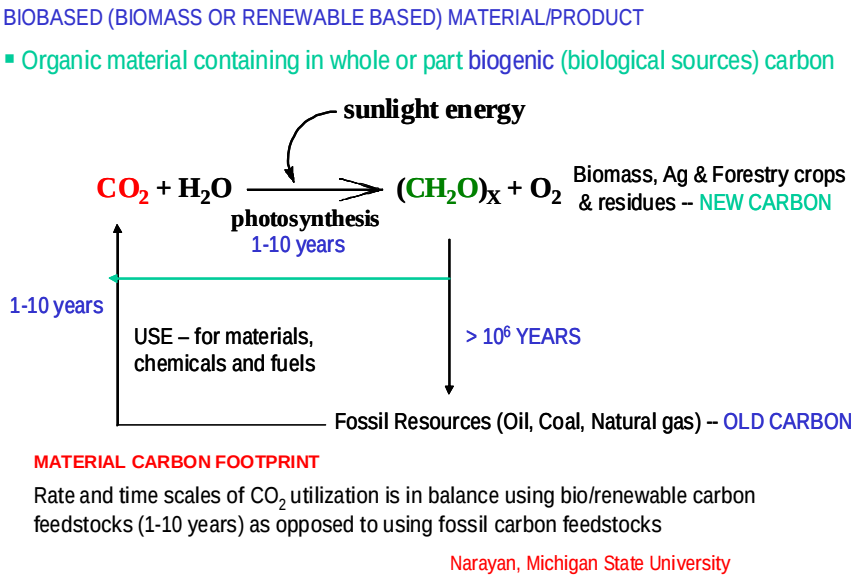
Organic material(s) are material(s) containing carbon based compound(s) in which the carbon is attached to other carbon atom(s), hydrogen, oxygen, or other elements in a chain, ring, or three dimensional structures (IUPAC – International Union of Pure and Applied Chemistry nomenclature)

Bio (carbon) content

The bio (carbon) content is based on the amount of biogenic carbon present, and defined as the amount of bio *carbon* in the material/product as fraction weight (mass) or percent weight (mass) of the total organic carbon in the material/product (ASTM D6866).

% bio or biobased (carbon) content = Bio (organic) carbon/total (organic carbon) * 100

ASTM D6866 Standard Test Methods for Determining the Biobased Content of Solid, Liquid, and Gaseous Samples Using Radiocarbon Analysis



The above standard and definitions are adopted by the US Government (the biopreferred program; www.biopreferred.gov); The European Union's lead market initiatives in the biobased products space have also adopted the above definitions and standards. Japan, India, and China have implemented the above definitions and standards as well.

References:

1. ASTM International, (2008), Committee D20 on Plastics, Subcommittee D20.96 on Biobased and Environmentally Degradable Plastics; www.astm.org,
2. ASTM International, (2007) Annual Book of Standards; Standards D 6866; D6400, D6868, D7021 ASTM International, Philadelphia, PA, Volume 8.03
3. Ramani Narayan, Biobased & Biodegradable Polymer Materials: Rationale, Drivers, and Technology Exemplars; ACS (an American Chemical Society publication) Symposium Ser. 939, Chapter 18, pg 282, 2006; Polymer Preprints (American Chemical Society, Division of Polymer Chemistry) (2005), 46(1), 319-320

Briefing Paper -- Value Proposition for Using Biobased Materials/Products

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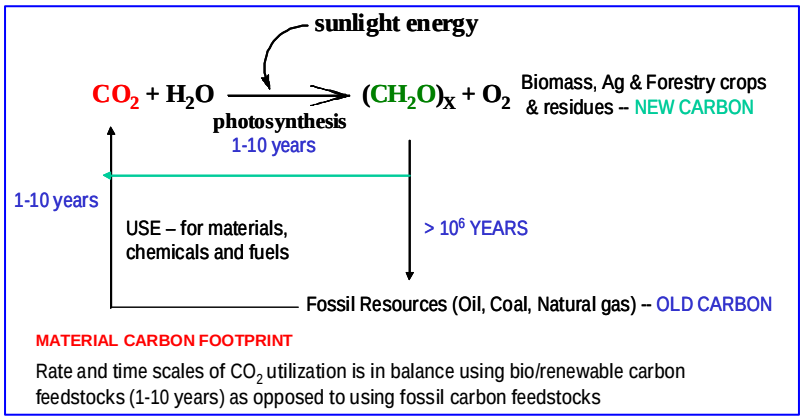
The fundamental value proposition for using bio/renewable carbon feedstock (as opposed to petro/fossil carbon feedstock) to manufacture biobased plastics or products is to **reduce the product's carbon footprint**

Scientific Basis for Reduced Carbon Footprint Using Bio/Renewable Feedstocks

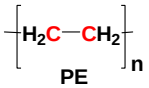
Carbon is the major basic element that is the building block of polymeric materials, fuels and even life itself. However, managing the carbon cycle has become the burning issue of today. There is increasing concerns over the growing man-made CO_2 emissions released into the environment with no offsetting fixation and removal of the released CO_2. Reducing our carbon footprint and addressing the carbon cycle imbalance is the major challenge facing us. The use of annually renewable bio feedstocks for manufacture of plastics and products offers an intrinsic zero or neutral carbon footprint value proposition.

Carbon is present in the atmosphere as inorganic carbon in the form of CO_2. The current levels of CO_2 in the atmosphere are around 380 ppm (parts per million). This life sustaining heat trapping value of CO_2 in the atmosphere (maintains the earth's temperature) is changing to life threatening because of increasing man made carbon (CO_2) and other heat trapping gas emissions to the atmosphere. While, one may debate the severity of effects associated with this or any other target level of CO_2, there can be no disagreement that uncontrolled, continued increase in levels of CO_2 in the atmosphere will result in a slow perceptible rise of the earth's temperature, global warming and with it associated severity of effects affecting life on this planet as we know. It is therefore prudent and necessary to try and maintain current levels – the "zero carbon emissions" approach. As can be seen from above scheme, the rate and time scales of CO_2 sequestration to petroleum/fossil feedstocks is in millions of years while the end-of-life rate and time scales of release into the environment is in 1-10 years. The math is simple; this is not sustainable and results in more CO_2 release than fixation, resulting in increased carbon emissions with it the attendant global warming and climate change problems. Again, from the figure, we can see that using renewable biomass crops as feedstocks to manufacture our carbon based products; the CO_2 released at the end-of-life of the product is captured by planting new crops or biomass plantations. Specifically, the rate and time scales of CO_2 release to the environment at end-of-life equals the rate of photo synthetic CO_2 fixation by the next generation crops or biomass planted – a net "zero carbon" foot print

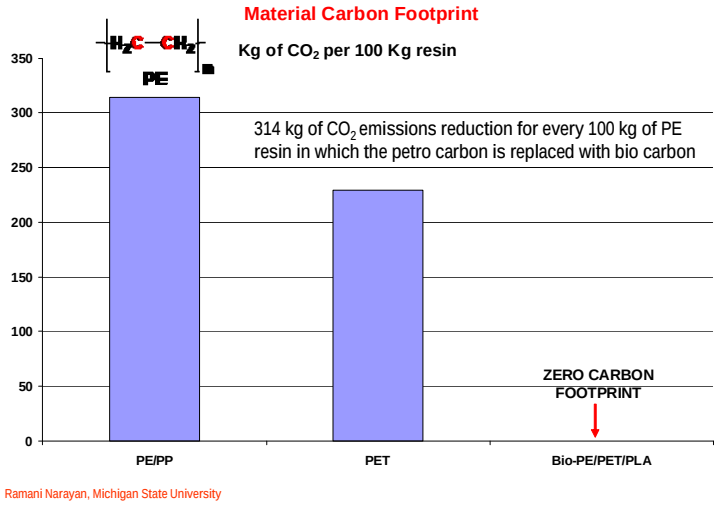


Applications to Materials -- Material Carbon Footprint

From a materials perspective, replacing the petro carbon in polyethylene with a bio carbon results in 314 kg of CO_2 emissions reduction for every 100 kg of polyethylene resin produced. As can be seen from the PE structure, there are 85.7 kg of carbon present

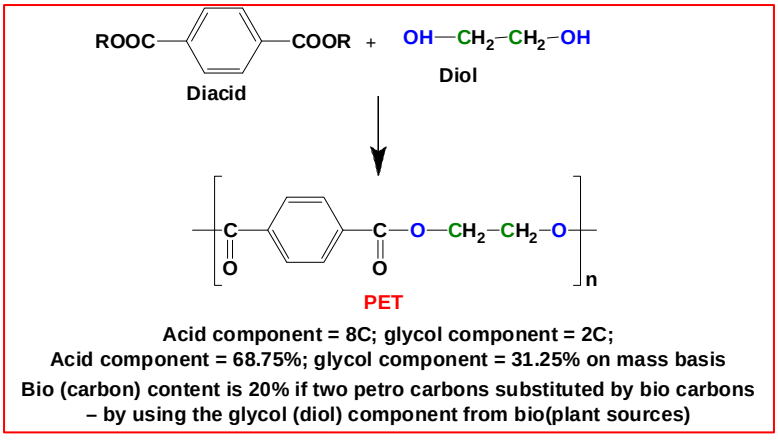


per 100 kg of polyethylene product, which results in 314 kg of CO_2 emissions. If the petro carbon is substituted by bio carbon, then there would be the same 314 kg of CO2 emissions released, however those CO_2 emissions are sequestered by the next biomass plantation as discussed earlier – the rate and time scales of CO_2 release is in the same phase as the rate and time scales of CO_2 sequestration, and there is no net CO_2 release from the material carbon present in the product. The attached figure schematically captures the material carbon footprint reductions by switching the origins of the carbon in polyethylene from petro/fossil feedstock to bio feedstock.



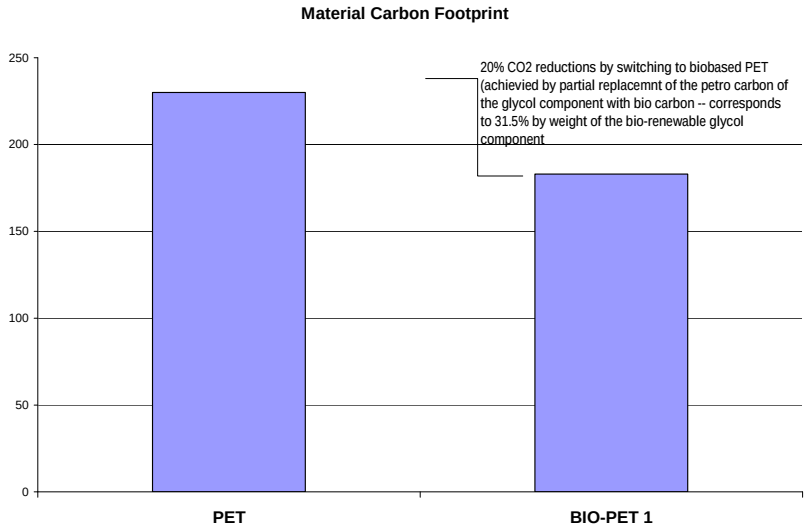
Substituting petro carbon partially with bio carbon – the case of bio-PET

PET (polyethylene terephthalate) used for manufacture of bottles comprises 10 carbon atoms (62.5% carbon) for every molecule of PET. It is synthesized or produced by condensation polymerization of terephthalic acid/ester (acid component, having 8 carbon atoms for every molecule) with ethylene glycol (glycol component, having 2 carbon atoms for every molecule). Replacing two petro carbons from only the glycol component with bio carbons results in a 20% reduction in CO_2 emissions relating to the materials used to produce PET is achieved by. Considering that the world wide use of PET resin for bottles and fiber is 37.5 million metric tons, this first step of replacing the glycol petro carbon with bio carbon offers a potential annual CO_2 reduction of 17.19 million metric tons. To visualize this CO_2 reduction in practical ready-to-understand terms the following equivalency applies (www.epa.gov equivalency calculator):



- Eliminate CO2 emissions from driving 3 million passenger vehicles each year

- eliminating the CO2 emissions from consuming 1,951,191,82 gallons of gasoline each year
- eliminating the CO2 emissions from consuming 40 million barrels of oil each year
- eliminating the CO2 emissions from using electricity in 2,384,189 homes each year



The above analysis discusses only the material carbon footprint reductions associated with incorporating bio carbon content into the polymer materials used to make polyethylene (Dow, and Braskem) and polyethylene terephthalate (PET). Coca Cola recently announced introducing "plant bottle" containing up to 20% bio carbon content using glycol from bio/plant feedstocks.

Process Carbon footprint -- LCA

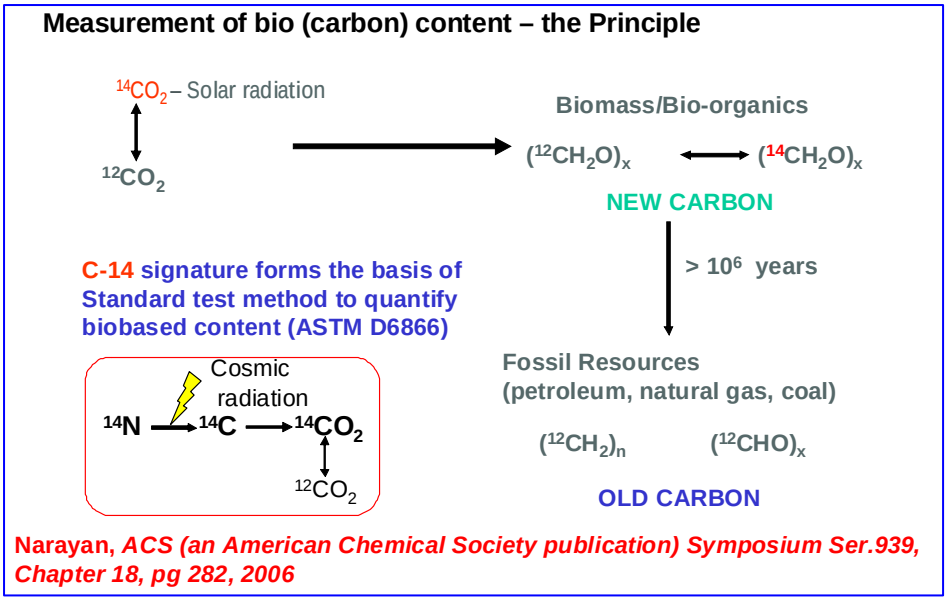
Additional CO_2 emissions reductions can potentially be realized in the process of converting the bio feedstock to the resin (the process carbon footprint) and other related activities like use and end-of-life disposal. This process carbon footprint can be calculated by using LCA (life cycle assessment) methodology. Typically, the process carbon footprint (based on ISO 1440 LCA standards methodology) for manufacture of biobased materials/products are better than existing process carbon footprints using petro/fossil feedstocks.

Measuring Bio (Carbon) Content

Biobased materials may contain 100% biogenic carbon (new carbon) or be mixed (physically, chemically, or biologically) with fossil/petroleum based carbon (old carbon). Therefore, one needs to define biobased content **– the amount of biogenic carbon present in the product.**

As shown in the attached figure, ^{14}C signature forms the basis for identifying and quantifying biboased content. The CO_2 in the atmosphere is in equilibrium with radioactive $^{14}CO_2$. Radioactive carbon is formed in the upper atmosphere through the effect of cosmic ray neutrons on ^{14}N. It is rapidly oxidized to radioactive $^{14}CO_2$, and enters the Earth's plant and animal lifeways through photosynthesis and the food chain. Plants and animals which utilise carbon in biological foodchains take up ^{14}C during their lifetimes. They exist in equilibrium with the ^{14}C concentration of the atmosphere, that is, the numbers of C-14 atoms and non-radioactive carbon

atoms stays approximately the same over time. As soon as a plant or animal dies, they cease the metabolic function of carbon uptake; there is no replenishment of radioactive carbon, only decay. Since the half life of carbon is around 5730 years, the fossil feedstocks formed over millions of years will have no ^{14}C signature. Thus, by using this methodology one can identify and quantify biobased content. ASTM subcommittee D20.96 codified this methodology into a Standard ASTM D6866.



D6866 test method involves combusting the test material in the presence of oxygen to produce carbon dioxide (CO_2) gas. The gas is analyzed to provide a measure of the products $^{14}C/^{12}C$ content and relative to the modern carbon-based oxalic acid radiocarbon Standard Reference Material (SRM) 4990c, (referred to as HOxII).

The carbon product is combusted to provide CO2, which is analyzed for the $^{14}C/^{12}C$ ratio. The $^{14}C/^{12}C$ ratio is compared directly with an oxalic acid radiocarbon standard reference material (SRM 4990c) that is 100% new (bio) carbon – actually 0.93 of the reference material to correct for the post 1950 ^{14}C injection into the atmosphere by nuclear testing.

Three different methods can be used to obtain the $^{14}C/^{12}C$ ratio, and documented in detail in the Standard – ASTM D6866.

References

1. *Ramani Narayan, Biobased & Biodegradable Polymer Materials: Rationale, Drivers, and Technology Exemplars; ACS (an American Chemical Society publication) Symposium Ser. 939, Chapter 18, pg 282, 2006;* Polymer Preprints (American Chemical Society, Division of Polymer Chemistry) (2005), 46(1), 319-320
2. *Ramani Narayan, Rationale, Drivers, Standards, and Technology for Biobased Materials; Ch 1 in Renewable Resources and Renewable Energy, Ed Mauro Graziani & Paolo Fornasiero; CRC Press, 2006*
3. *Ramani Narayan, Principles and Concepts of biomass based plastics and biodegradable plastics in "White biotechnology: High technology of energy and material" Ed. Y.Kimura and H.Ohara, CMC Publishing, Japan, 2008, pg 278*