MICHIGAN STATE UNIVERSITY

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RN

Using renewable (bio) content and bio-degradability to design and synthesize "green" products

Carbon footprint reduction and end-of-life strategies

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GREEN CHEMISTRY PRINCIPLES

Green chemistry Principle 4

- **Use renewable feedstocks:** Use raw materials and feedstocks that are renewable rather than depleting. Renewable feedstocks are often made from agricultural products or are the wastes of other processes; depleting feedstocks are made from fossil fuels (petroleum, natural gas, or coal) or are mined

Green Chemistry Principle 12

- **Design chemicals and products to degrade after use:** Design chemical products to break down to innocuous substances after use so that they do not accumulate in the environment.
- **Design chemicals and products to biodegrade after use:**

Framing the question – What is this all about?

- **Managing Carbon is the burning issue of the day!**
  - What are you doing to reduce your products (company's) carbon footprint?
  - What are you doing to reduce your products environmental footprint?

Carbon footprint reductions = CO_2 reductions = global warming/climate change issues

- **CARBON FOOTPRINT VALUE PROPOSITION**


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Value proposition for biobased plastics/products - Green Chemistry Principle 4 -

Using bio/renewable feedstock (as opposed to petro/fossil feedstock) to manufacture plastic products (biobased or biomass based plastics) reduces product's carbon footprint by:

- Lowering heat trapping CO_2 emissions
- Minimizing global warming/climate change problems


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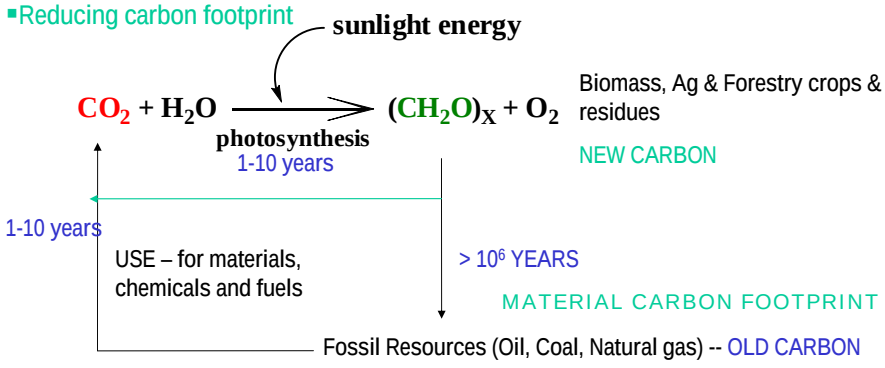
Terminology: Fundamentals, & Rationale

BIOBASED (BIOMASS OR RENEWABLE BASED)

- Organic material containing in whole or part biogenic (biological sources) carbon
- Refers to using biomass or crop feedstock (New carbon) vs petroleum or fossil feedstock (Old carbon)
- Reducing carbon footprint



Rate and time scales of CO_2 utilization is in balance using bio/renewable feedstocks (1-10 years) as opposed to using fossil feedstocks

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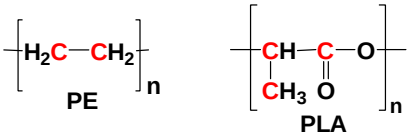
Carbon footprint contributions divided into:

- **MATERIAL/PRODUCT CARBON FOOTPRINT**



Impact of switching from petro/fossil carbon to bio carbon

- **PROCESS CARBON FOOTPRINT**
  - **Carbon emissions from all stages of unit operations to convert the selected C-feedstock (petro or bio/renewable) to product**
  - **Material (Carbon) balance – life cycle inventory analysis (LCI)**
  - **Impact on the environment of the carbon emissions – global warming potential (GWP)**

- **Environmental Footprint (LCA methodology)**
  - **Carbon footprint + other impact footprint categories like human health, ozone depletion, eutrophication, acidification, photochemical smog, etc**

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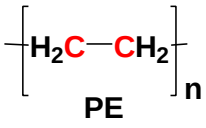
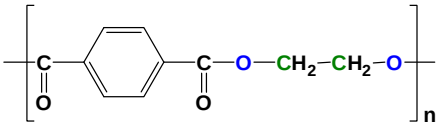
Material Carbon Footprint

What is the impact of the material/product's carbon footprint on the environment ?

- 100 Kg of polyethylene will result in net ?? Kg of CO_2 released into the atmosphere
- 100 Kg of bio polyethylene will result in net ?? Kg of CO_2 released into the atmosphere
- 100 Kg of polyester (PET – assume C2 glycol and C8 terephthalic acid will results in net ?? Kg CO_2 release into the atmosphere
- 100 Kg of 100% biobased PET will result in net ?? Kg release into the atmosphere



PE



PET

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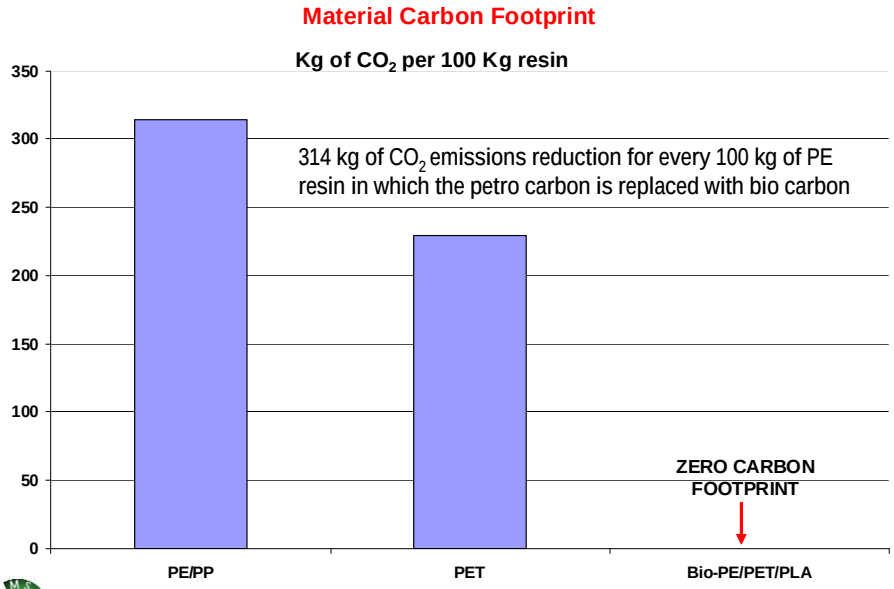
Material Carbon Footprint



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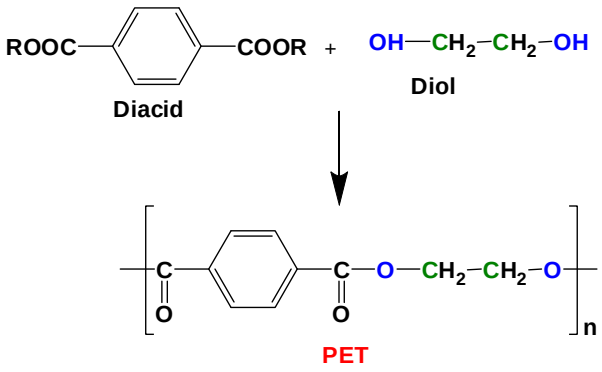
Material carbon footprint calculations – PET exemplar



Acid component = 8C; glycol component = 2C; biocontent is 20%

Acid component = 68.75%; glycol component = 31.25% on total mass basis

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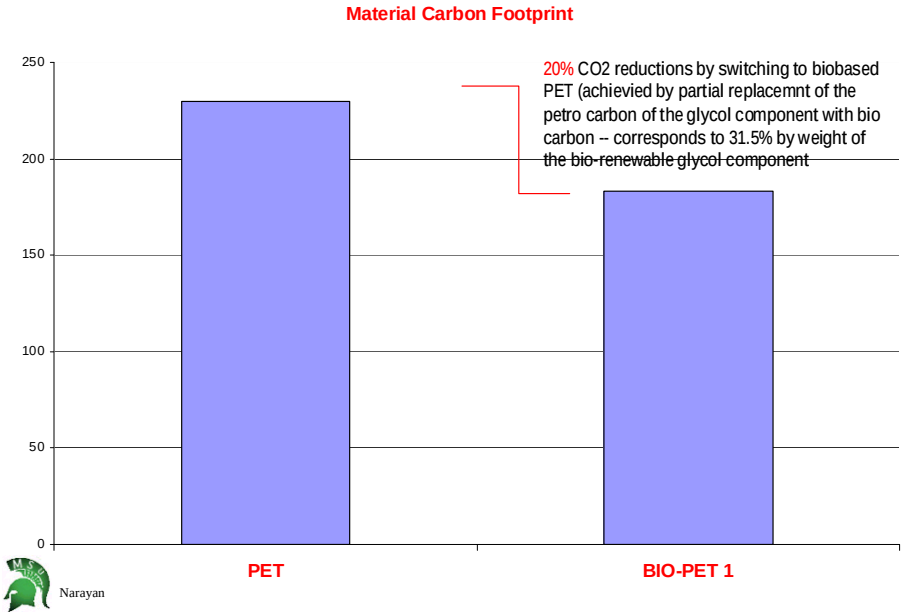
Material carbon footprint calculations – PET exemplar



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Communicating and presenting CO_2 emissions reduction data – "material carbon" footprint

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 an annual CO2 reduction of 17.19 million metric tons. To visualize this CO2 reduction in practical ready-to-understand terms the following equivalency applies (equivalency calculator):

- Eliminate CO2 emissions from driving 3 million passenger vehicles each year
- Eliminate CO2 emissions from consuming 1,951,191,82 gallons of gasoline each year
- Eliminate CO2 emissions from consuming 40 million barrels of oil each year
- Eliminate CO2 emissions from using electricity in 2,384,189 homes each year

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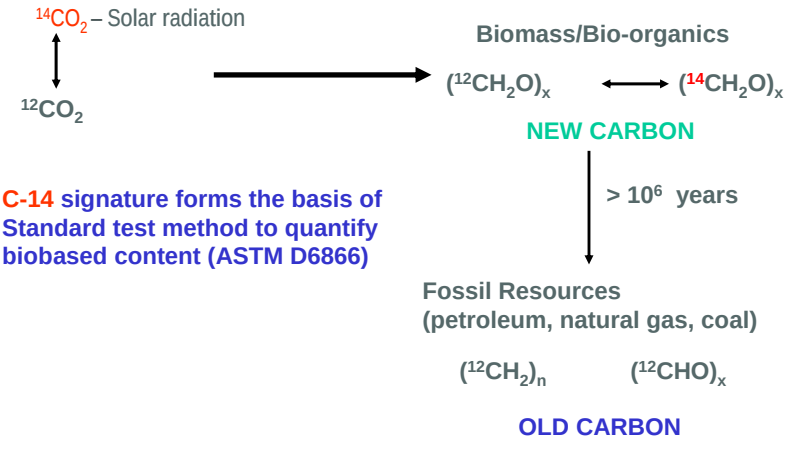
GHG, equivalency calculator; www.epa.gov

Measurement of bio (carbon) content – the Principle



C-14 signature forms the basis of Standard test method to quantify biobased content (ASTM D6866)

Narayan, *ACS (an American Chemical Society publication) Symposium Ser.939, Chapter 18, pg 282, 2006*

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Measurement of bio (carbon) content – ASTM D6866

C-product combusted to CO_2

$^{14}C/^{12}C$ ratio is compared directly with a 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.

14.27 dpm/g is the absolute value of the primary oxalic acid standard (SRM 4990b)

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Biobased Carbon Content Determination

Amount of biobased *carbon* in the material or product as fraction weight (mass) or percent weight (mass) of the total organic carbon in the material or product.

$$\%\ \text{BIO or BIOBASED CONTENT} = \frac{\text{BIO (Organic) CARBON}}{\text{TOTAL (Organic) CARBON}} * 100$$

- On a carbon basis, not weight or mole or any other measure.
- Reducing carbon foot print is the driver for using a bio/renewable feedstock (new carbon) -- not oxygen or nitrogen or anything else
- So biocarbon content is the correct measurement metric

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Process Carbon Footprint – Use LCA methodology Fundamental ChE Material & Energy Balances

- Draw process flow chart – define system and system boundaries
  - Cradle to business gate, but include use and end-of-life units
  - Data quality important
- Write the material balance equations and solve
- Assign output emission streams to selected impact categories like global warming, acidification, human health, ecotoxicity, eutrophication (ASTM D7075, EPA model)
- Calculate the impact, and normalize to the per year per capita North American emissions for the selected impact category

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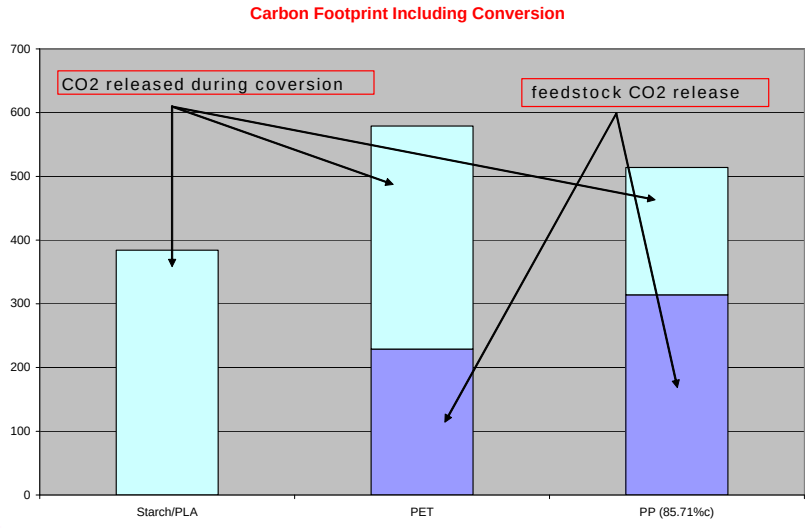
Process Carbon Footprint – the LCA trap



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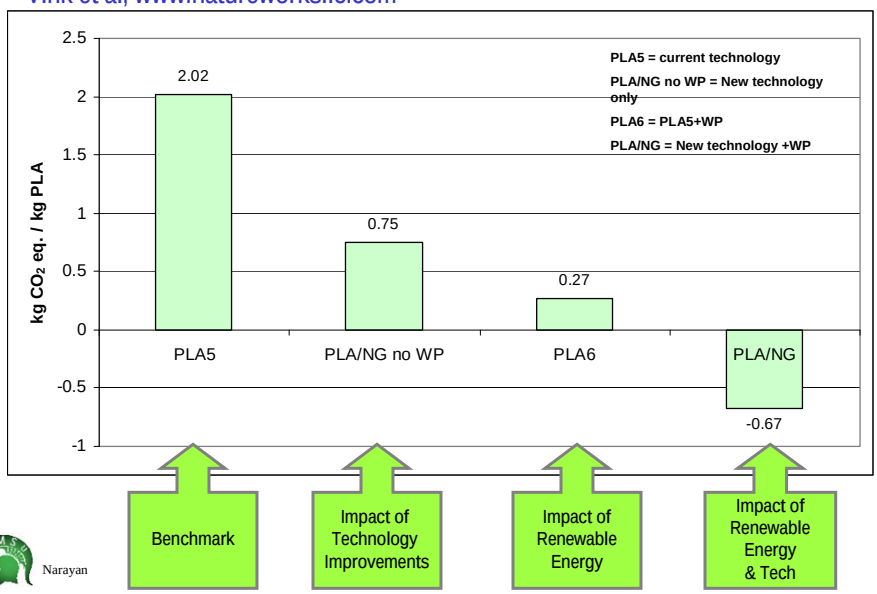
Results of the utilization of renewable energy and new technology on GHG

Vink et al, www.natureworksllc.com



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END-OF-LIFE OPTION – Green Chemistry Principle 4

Value proposition for biodegradable plastics/products

- **Using biodegradability as an end-of-life option to remove single use short life disposable plastics/products from the environmental compartment completely and in a safe and efficacious manner via microbial assimilation (microbial food chain)**
  - **Disposal environment (like composting, anaerobic digestor, marine**
  - **Time to complete biodegradation**
    - **90%+ of the carbon substrate should be completely assimilated by the microorganisms present in the disposal within a short time period (one year or less)**
  - **Degradable, partial biodegradable not acceptable – serious health and environmental consequences**

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Biodegradability under composting condiitons

- **Specification Standards ASTM D6400, D6868, D7021**
- **Specification Standards EN 13432 (European Norm)**
- **Specification Standards ISO 17088 (International Standard)**

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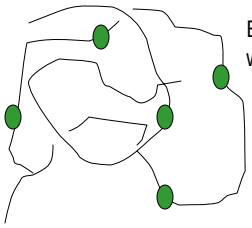
What does Biodegradable Mean?

Can the microorganisms in the disposal system (composting, soil, anaerobic digestor) assimilate/utilize the carbon substrate as food source completely and in a short defined time period?

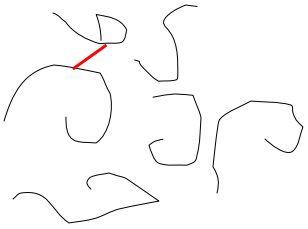


Environment – soil, compost, waste water plant, marine

Hydrolytic

oxidative

Enzymatic



Oligomers & polymer fragments

Polymer chains with susceptible linkages

Biodegradation: Only if all fragmented residues consumed by microorganisms as a food & energy source

Define time and environment (disposal system)

Complete microbial assimilation

defined time frame, no residues!!!

$CO_2 + H_2O$ + Cell biomass

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Measuring biodegradability

Microorganisms extract chemical energy for use in their life processes by the aerobic oxidation of glucose and other utilizable substrates – BIODEGRADBLE PLASTICS, food waste, paper, forest residues biological matter

AEROBIC

Glucose/C-bioplastic + 6 O_2 → 6 CO2 ↑ + 6 H2O; $DG^{0'}$ = -686 kcal/mol

ANAEROBIC

Glucose/C-bioplastic → 2 lactate; $\Delta G^{0'}$ = -47 kcal/mol

→ CO_2 + CH_4 ↑

CO_2 is the quantitative measure of the ability of the microrganisms present in the disposal environment to utilize/assimilate the test C-bioplastic, which is the sole C-source available for the microorganisms -- biodegradation/bioassimilation

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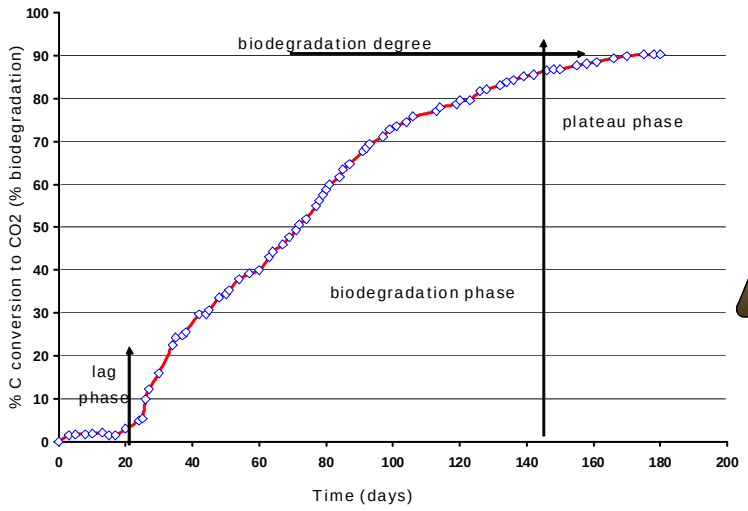
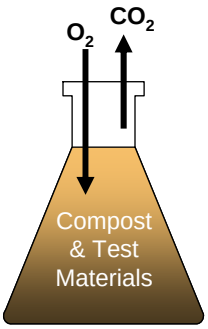
Measuring biodegradability





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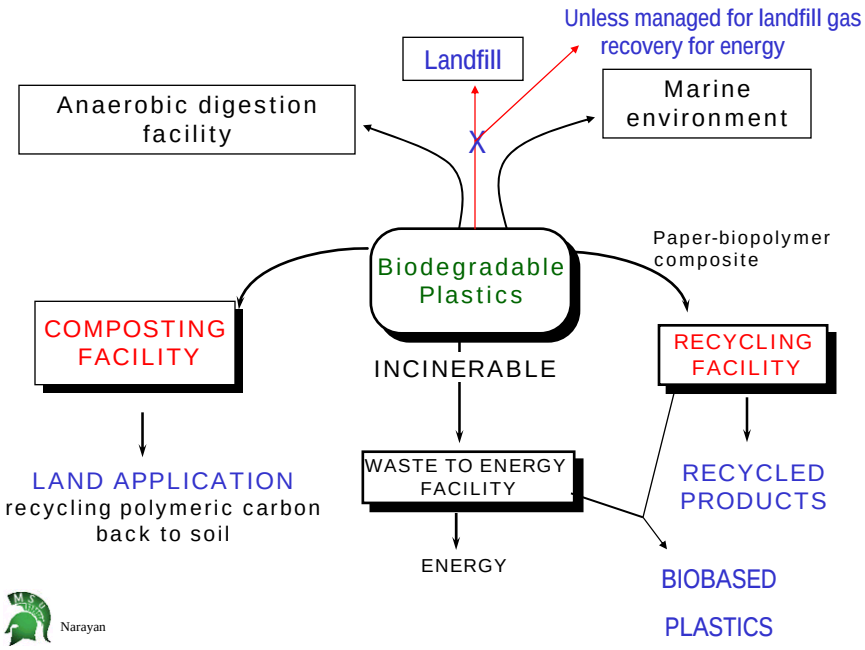
END OF LIFE OPTIONS



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MISLEADING CLAIMS – UNSUPPORTED BY DATA

Oxo-biodegradable polyethylene (PE) film claims – *"The technology is based on a very small amount of prodegradant additive being introduced into the manufacturing process, thereby changing the behavior of the plastic and the rate at which it degrades. The plastic does not just fragment, but is then* ***consumed by bacteria and fungi and therefore continues to degrade to nothing more than carbon dioxide, water and biomass*** *with no toxic or harmful residues to soil, plants or macro-organisms"*

"Designed to interact with the microorganisms present in landfills, composters, and almost everywhere in nature including oceans, lakes, and forests. These microorganism ***metabolize the molecular structure of the plastic breaking it down into soil****"*

"Combined with an oxo-biodegradable proprietary application method to produce films for bags. This product, when discarded in soil in the presence of microorganisms, moisture, and oxygen, ***biodegrades, decomposing into simple materials found in nature****. Completely breakdown in a landfill environment in 12-24 months leaving no residue or harmful toxins and have a shelf life of 2 years"*

In each of the above cases scientific substantiation showing carbon conversion to CO_2 using established standard test methods NOT PROVIDED

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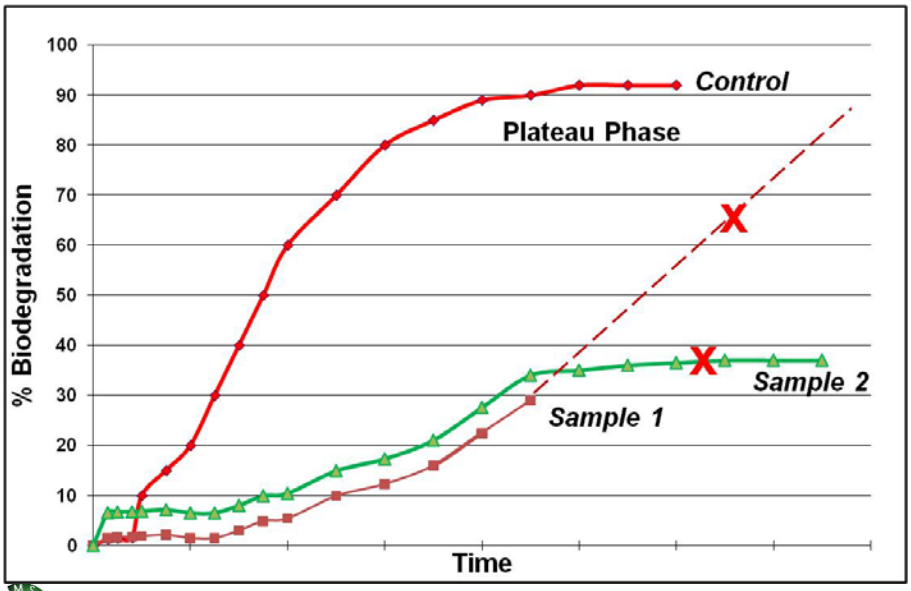
MISLEADING BIODEGRADABILITY CLAIMS



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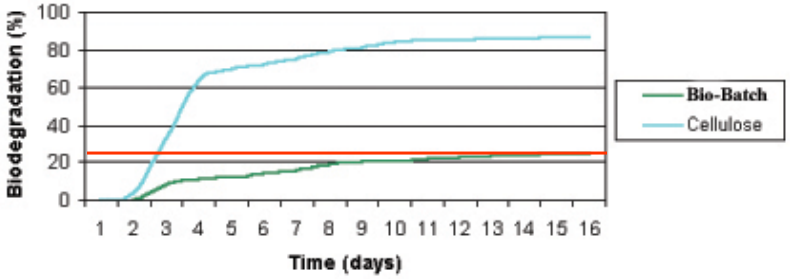
Green Washing Claims -- Additive Technology

- *"Plastic products with our additives at 1% levels will fully biodegrade in 9 months to 5 years wherever they are disposed like composting, or landfills under both aerobic and anaerobic conditions"*



The 50% Bio-Batch film did not degrade as completely or as quickly as the cellulose. At the end of the test, 19% of the film had degraded.

The results of the aerobic degradation tests indicate that, in time, plastics produced using Bio-Batch pellets will biodegrade in aerobic conditions.

DATA DOES NOT SUPPORT THE CONCLUSIONS!

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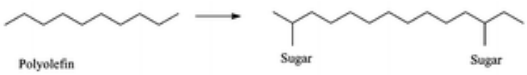
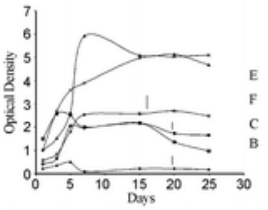
BIODEGRADABILITY CLAIMS

- *Chem. Commun.*, 2002, (23), 2884 - 2885
  - A hypothesis was developed, and successfully tested, to greatly increase the rates of biodegradation of polyolefins, by anchoring minute quantities of glucose, sucrose or lactose, onto functionalized polystyrene (polystyrene-co-maleic anhydride copolymer) and measuring their rates of biodegradation, which were found to be significantly improved
- PRESS
  - Sugar turns plastics biodegradable. Bacteria make a meal of sweetened polythene and polystyrene.





Increase in rates of biodegradation for sugar linked polystyrene

weight loss of only 2-12%,

Only sugar is being assimilated, PE chain intact – Is this a genuine example of biodegradable plastic?

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Serious consequences with degradation as wellas incomplete and partial biodegradation

- **plastic pieces can attract and hold hydrophobic elements like PCB and DDT up to one million times background levels. As a result, floating plastic is like a poison pill**
- **PCBs, DDE, and nonylphenols (NP) were detected in high concentrations in degraded polypropylene (PP) resin pellets collected from four Japanese coasts.**
- **Plastic residues function as a transport medium for toxic chemicals in the marine environment.**
  - **Takada et al Environ. Sci. Technol. 2001, 35, 318-324**
  - **Blight, L.K. & A.E. Burger. 1997. Occurrence of plastic particles in seabirds from the Eastern North Pacific. Mar. Poll. Bull. 34:323-325**
  - **From Algalita Marine Research Foundation – www.algalita.org/pelagic_plastic.html**

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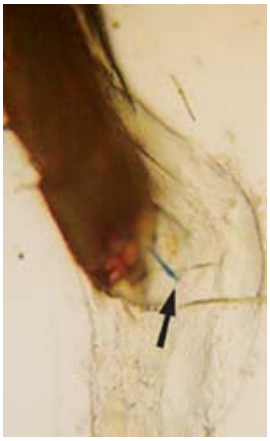
THE NEED FOR COMPLETE BIODEGRADABILITY !

- Thompson, R.C. et al. 2004. Lost at sea: Where is all the plastic? Science 304, 838, 2004
- Plastic debris around the globe can erode (degrade) away and end up as microscopic granular or fiber-like fragments, and that these fragments have been steadily accumulating in the oceans
- fragments come from several sources, the researchers suggest. These include mechanical erosion of nondegradable plastic bottles and packaging, nondegradable parts of biodegradable plastics, and plastic pieces used as abrasives in cleaning agents.



FLOTSAM Lab experiments show that marine animals consume microscopic bits of plastic, as seen here in the digestive tract of an amphipod. © *Science* 2004

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Technology exemplars

- **Merquinsa have introduced TPU grades with bio content ranging from 30 to 75% (measured as per ASTM D6866)**
- **Cargill introduced BiOH^{TM}Polyols with essentially 100% biocarbon content that have been used in PU foam products giving 12 and 17% bio content**
- **Ford developed and introduced biobased PU foam for use in in the 2008 Mustang seat cushion, seat cover**
- **DuPont introduced biobased Sorona (polyester), and Cerenols (polyols)**
- **Coca Cola announced the introduction of Bio-PET (plant bottle)**
- **India Glycols offers biobased polyols derived from molasses via ethanol**

Polyol component has been the one used for introducing bio content.

At MSU, we have used a single stage room temperature ozonation process to manufacture bio polyols.

We are researching the manufacture of the isocyanate component

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BIO PRODUCT TECHNOLOGY EXEMPLARS

- DuPont's 1,3-PDO ---- polyesters (Sorona) & renewably sourced products like Hytrel thermoplastic elastomers, Cerenol polymers
- NatureWorks –40,000 t (300 MM lbs) PLA
- PURAC – Lactic, lactide, Thailand (100,000 t)
- BASF – 14, 000 t biodegradable polyesters – biobased polyesters incorporating PLA; 60,000 t plant 2010)
- Novamont -- Bioresins
- Natur-Tec -- Bioresins
- Braskem (100 MM lbs), DOW (250 MM lbs)
- Solvay – 60, 000 tons ethylene, 110, 000 t EtOH PVC
- ADM-Metabolix – Polyhydroxyalkanoates (PHA's)
- Arkema – Polyamide 11 – high performance polymers
- Biopolyurethanes – Ford, Toyota
- Biofiber composites – auto components
- BioPET --- Coca Cola's plant bottle
- Several others

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U.S. Farm Security and Rural Investment Act of 2002 (P. L. 107-171), Title IX Energy, Section 9002 FARM BILL

- Federal Procurement of Biobased Products – the "biopreferred program" (www.biopreferred.gov)
  - develop guidelines for designating biobased products
  - publish a list & issue criteria for a designated biobased products list (DBL) for federal purchase;
- Includes:
  - Definition, content verification, ASTM D6866
  - environmental profile using LCA – ASTM Standard
    - ASTM D7075 "Standard practice for evaluating and reporting environmental performance of biobased products". -- LCA TOOLS/BEES analysis
  - Biodegradability using ASTM D6400 and D6868 (paper coatings) D7021 (marine)
  - performance requirements; and
  - assurance that products are available.

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Summary – Learning Objectives Check

- **Incorporating bio content offers value proposition for reducing material carbon footprint and potentially process carbon footprint as well as environmental footprint (use renewable energy, reduced weight and other options)**
- **Understand the concepts of material carbon footprint & process carbon footprint,**
- **Understood the testing methods and standards to identify and measure bio-content of products**
- **Learnt to calculate carbon footprint (CO_2) reductions using bio content analysis**
- **Learnt the process carbon footprint calculations using LCA methodology, but more importantly not to get into the LCA trap – clearly identify boundary conditions**
- **Understood biodegradability and End of Life Issues and the difference between biodegradability and bio based**
- **Beware of biodegradability claims – verify with data**


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Entrepreneurship – an important learning for Scientists & Engineers
Experiences of a Faculty Entrepreneur in the BioPlastics Space

MICHIGAN STATE UNIVERSITY

BIOENTERPRISES

Biopolymer Innovations
www.biopolymerinnovations.com

KTM GREENCELL BIODEGRADABLE ENGINEERED FOAM
www.ktmindustries.com

BIOPLASTIC POLYMERS & COMPOSITES
www.bioplasticpoloymers.com

Zeeland Biobased Products LLC
www.zfsinc.com

Spartans Biofuels LLC

BIOBASED MATERIALS RESEARCH GROUP

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University Distinguished Professor
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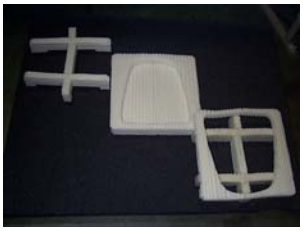
Entrepreneurial BIOENTERPRISES

- 21 issued patents, 7 pending published patents, and 6 filed patents, and 125 peer reviewed publications
- Biobased materials technology platform covered by the issued and pending patents have been licensed or resulted in a spin-out company
- Biofuels technology as a bolt-on to major players
- Eight technologies have been licensed or resulted in a spin-out company

Entrepreneurial BIOENTERPRISES

- MSU project on "biobased foam materials for protective packaging applications and for craft and toy markets" . KTM employs 11 people with sales revenue of $2 MM – business plans call for it to grow to to total revenues of $45 MM at the end of 5 years. MSU has a 2% of net sales royalty bearing patent and technology support licensing agreement with KTM www.ktmindustries.com

TOYOTA



FOAM SHEETS READY FOR SHIPMENT

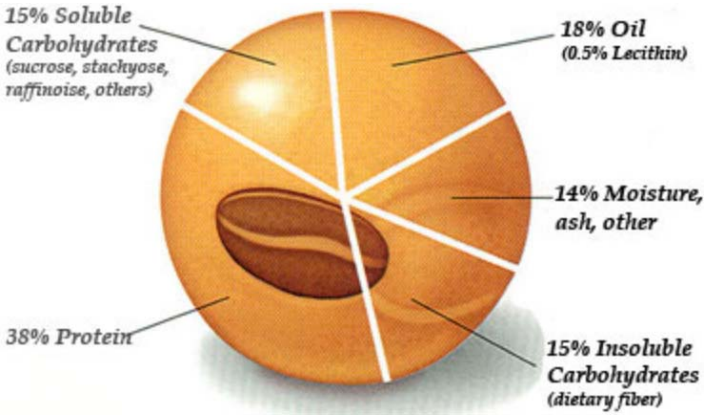
Entrepreneurial BIOENTERPRISE WITH

Zeeland Farm Services

www.zfsinc.com

- a family owned (Meeuwsen brothers) Michigan business with over 50 years of service to the agricultural and transportation industries
- 200 employees with an annual gross sales revenue of over $150 MM
- process about 26,000 bushels of soybeans per day, operating 24 hours a day, 360 days a year, to produce two primary products: soybean meal and soybean oil.
  - 90% of the total soybeans processed in the State is done at ZFS – largest soybean processor in MI
  - 2500 MI farmers are serviced and ZFS buys 99% of their soybeans from MI farmers
  - successful Michigan business against multi national competitors such as Bunge Cargill and ADM

Typical Soybean Composition



soybean meal

- is used to produce animal feed in poultry, swine, cattle, and aquaculture
- refined to soy flour, soy concentrates, and soy isolates

ZEELAND BIO-BASED PRODUCTS, LLC

ZFS Zeeland Farm Services, Inc. AND BIOPLASTIC POLYMERS & COMPOSITES

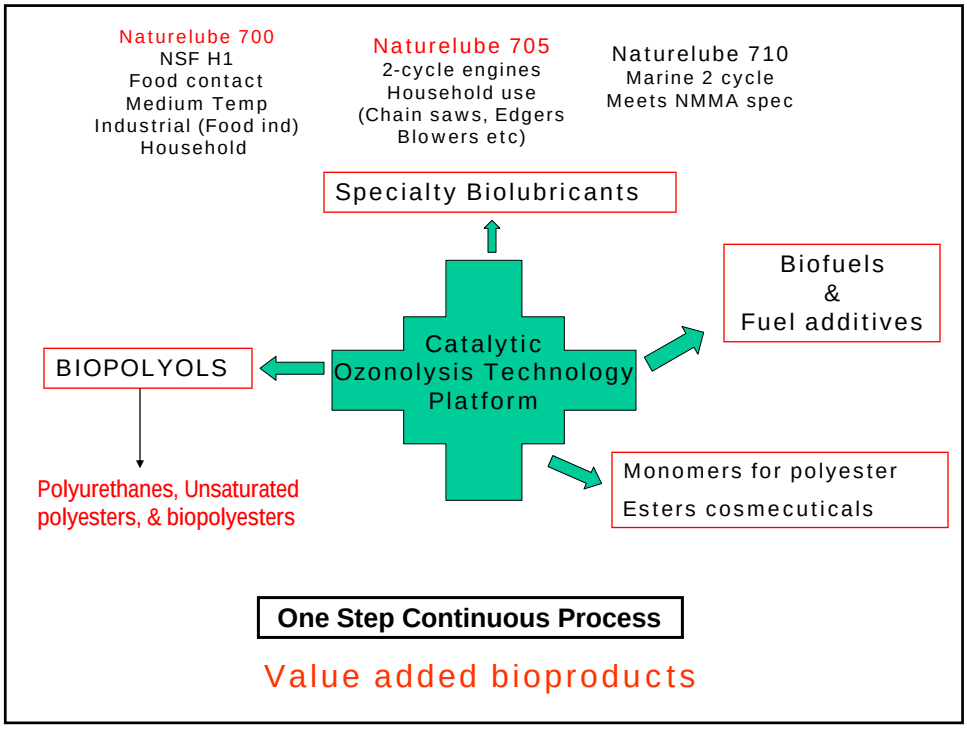
Initial Seed Funding of $ 1.02 million from

Michigan Economic Development Corporation (MEDC) 21st Century Jobs Fund Program

R&D cooperation & technical support → MICHIGAN STATE UNIVERSITY CHEMICAL ENGINEERING & MATERIALS SCIENCE

Manufacture in Michigan – sell world wide
"Valued Added Biobased Industrial Products & Chemicals

- Bio-Based, Thermally Stable and Biodegradable Lubricants
- Polyols for PU and UPR Resins
- Monomers for biopolyesters
- Esters for cosmecuticals
- Fuel Additives for Gasoline and Diesel

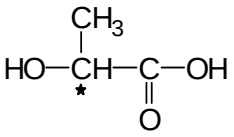


Entrepreneurial BIOENTERPRISES (Contd)
Licensed Technology Patents

- Corn Products International is one of the world's largest corn refiners. With net sales of $2.3 billion for 2004, the Company, through its company-owned operations, joint ventures, alliances and technical licenses, has 34 plants spanning 16 countries.
  - In 2005, Corn Products licensed our three filed patents (on modified starch, starch-polyester composite resins), and signed an agreement with MSU to commercialize the technology.
  - Introduced a biobased biodegradable plastic bag "ECOBRAS" based on the technology – JV between BASF and Corn Products -- www.cornproducts.com.br/ecobras
- BioPlastics Polymers & Composites licensed MSU technology for biobased and biodegradable films and molded products applications
  - In 2005, Northern Technologies International , a $100 million publicly traded micro cap company (NASDAQ: NTIC) formed a partnership with BioPlastic Polymers to commercialize the bioplastics technology world-wide branded it Natur-Tec

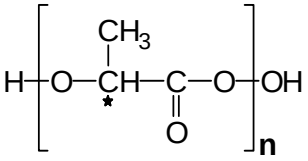
Ramani Narayan, Michigan State University, www.msu.edu/~narayan

Narayan Group Work on PLA



Lactic acid

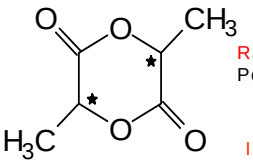
PLA TECHNOLOGY



PLA

Commercialized by
Natureworks LLC (Cargill-Teijin JV)

Reversible Kinetics and Thermodynamics of the Homopolymerization
Macromolecules, 30, 7075, 1997



Dilactide

Racemization Kinetics, ACS Polymer Preprints, 39(2), 86, 1998

Introduction to Properties, Engineering, and Prospects of Polylactide Polymers, D. Witzke, Ph.D. thesis, MSU, 1997

Free Radical Branching of Polylactide by Reactive Extrusion, Polymer Eng., & Sci., 38 (2), 311, 1998

Maleation of Polylactide (PLA) by Reactive Extrusion, J. Appl. Polym. Sci., 72, 477-485, 1999

SPARTAN BIOFUELS LLC

Advancing biofuels processing
&
New biofuels development

Dennis Miller and Ramani Narayan
millerd@egr.msu.edu narayan@msu.edu

COMPANY BACKGROUND

- Technology, expertise, and access to advanced biofuels manufacturing methods and novel biofuels compositions.
- Strategic partnerships
  - MSU/Professor's Miller and Narayan research group for new biofuels technology
  - Ford Motor Company for evaluation and cooperatively developing biofuels formulations
  - Zeeland, Michgan's largest soybean crusher for feedstock
- founding consortium member of the Michigan Biorefinery Training Facility (BTF) for the purpose of training Michigan and Midwestern U.S. workers for emerging bioeconomy-related industries

PARTNERSHIPS & PILOT PROJECT

- The company has partnership and cooperation with
  - Michigan State University, Ford Motor Company, and Zeeland Farm Services
  - founding consortium partner in a federally funded Biorefining Training Facility which is training Michigan and Midwestern U.S. workers for emerging bioeconomy-related industries
- CANOLA OIL PILOT PROJECT – supported by MSU
  - 200 acres of Canola (high oil yield crop) planted equivalent to 20,000 gallons of oil
  - Process at pilot Webberville facility to biodiesel, and supply MSU
  - Closed loop system, also establish use in higher value applications like lubricants and polyols (for polyurethane and polyester industrial applications)
  - Establish economics for biofuels and bioproducts from vegetable oil base --- canola, soybean