פלסטיקה ירוקה, עובדות וכיוונים עתידיים
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בניין מיטשל, ביה"ס הגבוה שנקר, רח' ידע עם, רמת-גן

שנקר בי"ס גבוה להנדסה ולעיצוב
איגוד יצרני הפלסטיקה והגומי בישראל
האגודה הישראלית לפולימרים ופלסטיקה

Bioplastics: Durable Renewable Sources Polymers

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What are bioplastics?

- Polymers based on renewable raw materials - bio/new carbon (ASTM D 6866, based on C14)
- Biodegradable polymers with approved biodegradability in compost (EN 13432, ASTM D 6400-99)
- Most of bioplastics are based on agricultural feedstocks

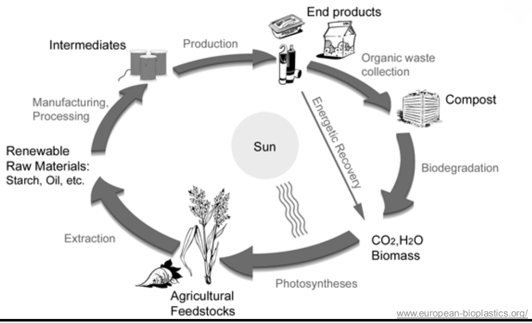
Why bioplastics?

- Depletion of fossil resources
- Synthetic plastics are building up in landfill
- Use of non-renewable sources contributes to global warming.
- Closing the carbon loop by composting and energetic recovery (biodegradable), bioplastics make a positive contribution to climate protection (CO_2 footprint).

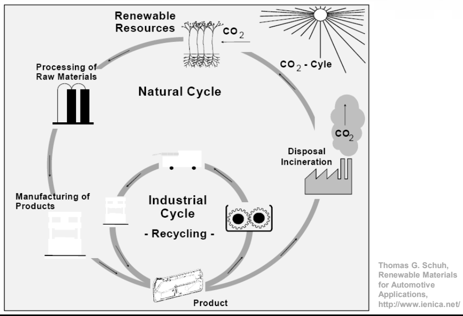
Bioplastics

- Biobased and biodegradable (PLA, PHA, starch): short-life, disposable products
- Biobased and durable (castor oil based Nylon, ethanol based green PE, soy based polyurethane)
- Remember: Biobased plastics are not always biodegradable and biodegradable plastics are not always biobased

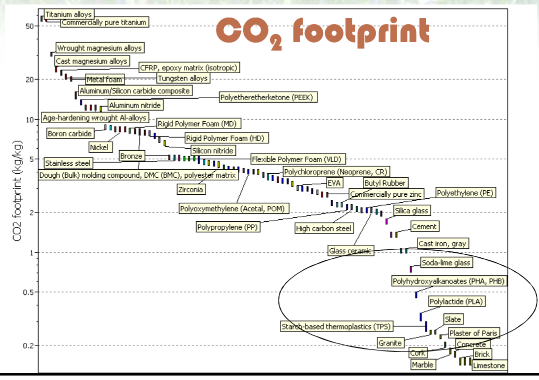
Biodegradable bioplastic life cycle (LCA)



Durable bioplastic life cycle (LCA)

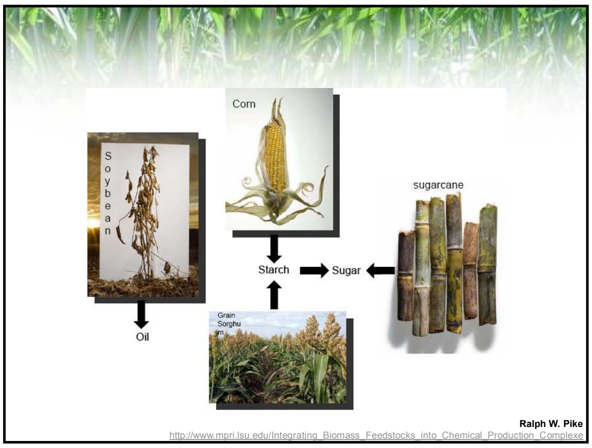


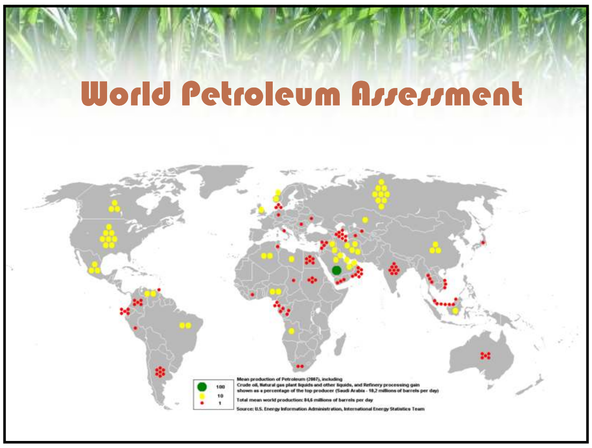
CO_2 footprint

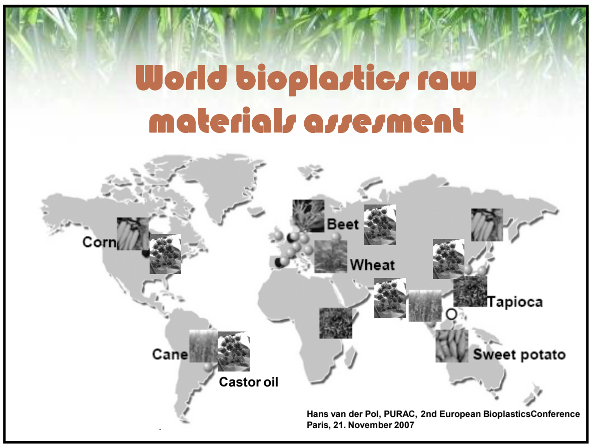


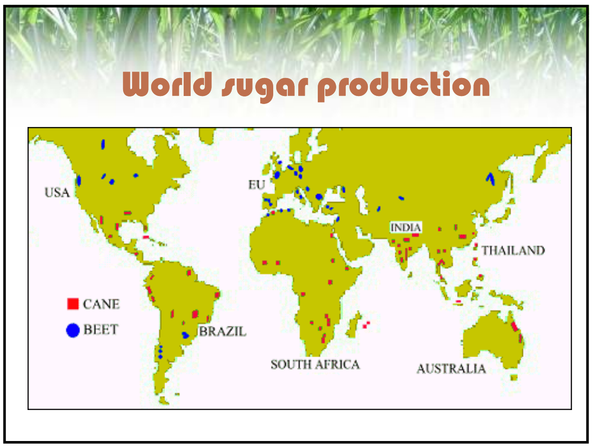
Raw Materials for Bioplastics

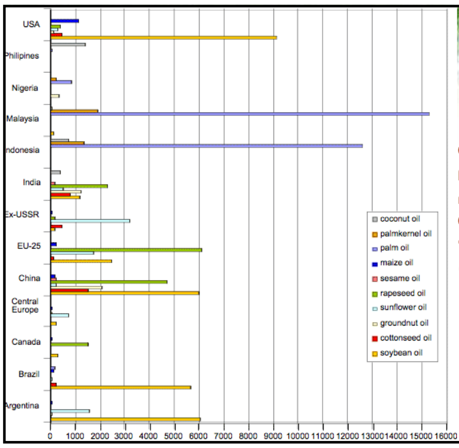
- **Sugar and starch bioproducts** obtained through fermentation and chemical processes and include **alcohols**, acids, starch and xanthium gum derived from feedstocks including **corn, sugarcane, sugar beets, rice, potatoes, sorghum grain and wood.**
- **Oil and lipid-based bioproducts** obtained through chemical processes and include fatty acids, oils alkyd resins and glycerin derived from feedstocks including **soybeans, castor oil, rapeseed and other oilseeds.**
- **Cellulose derivatives** and plastics including cellulose acetate (cellophane) and triacetate, cellulose nitrate, alkali cellulose and regenerated cellulose derived from wood pulp and cotton linters.
- **Protein**: chitin, soy protein, zein, wheat gluten, silk.
- **Biomass**


Corn
Soybean
sugarcane
Starch
Sugar
Oil
Grain Sorghum
Ralph W. Pike
http://www.mpri.lsu.edu/Integrating_Biomass_Feedstocks_into_Chemical_Production_Complexe


World Petroleum Assessment


World bioplastics raw materials assesment
Corn
Beet
Wheat
Tapioca
Cane
Castor oil
Sweet potato
Hans van der Pol, PURAC, 2nd European BioplasticsConference
Paris, 21. November 2007


World sugar production
USA
EU
INDIA
THAILAND
CANE
BEET
BRAZIL
SOUTH AFRICA
AUSTRALIA



Oils and fats Production by main Countries 2005/06 (1000 T)

www.fediol.be

Bioplastics instead of food?

- Can bioplastics contribute to the global food crisis by taking over large areas of land previously used to grow crops for human consumption???
- Solution: non-food crops for bioplastics raw materials on “set aside areas”
- “Set aside areas”: proportion of farmland out of production (created to rid Europe of the grain mountains of the 1980s, has been officially reduced to 0% this year by the EC)
- Set aside areas provides a sanctuary for beleaguered wildlife in the farmed landscape.
- The production of non-food crops has a long tradition in the European Community agriculture.

BioPreferred USA Program

- The Farm Security and Rural Investment Act (FSRIA) defined that "biobased products" are products determined by the U.S. Secretary of Agriculture to be commercial or industrial goods (other than food or feed) composed in whole or in significant part of biological products, forestry materials, or renewable domestic agricultural materials, including plant, animal, or marine materials.
- The USDA’s BioPreferred program creates an important market for these green products by requiring federal agencies to give purchasing preference to biobased products when available and comparable to petroleum-based products.

Non biodegradable durable bioplastics sources

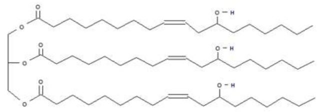
Natural oil polyols

- **Natural oil polyols**, also known as NOPs or biopolyols, are polyols derived from vegetable oils by several different techniques.
- There are a limited number of naturally occurring vegetable oils (triglycerides) which contain the unreacted hydroxyl groups that account for both the name and important reactivity of these polyols.
- **<u>Castor oil</u> is the only commercially-available natural oil polyol that is produced directly from a plant source: all other NOPs require chemical modification of the oils directly available from plants.**

Sources of natural oil polyols

www.cambridge2000.com

- Castor oil is made up of a mixture of fatty acid triglycerides containing over 85% of ricinoleic acid.
- The molecule of this acid has a linear chain comprising 18 carbon atoms.
- Steam cracking breaks it into two parts: one part consisting of 7 carbon atoms and the other of 11 carbon atoms.
- The major component of castor oil is composed of the tri-ester of rincinoleic acid and glycerin :



Castor oil based polyamides

Polyamide 11

- By amination of the C11 acid from castor oil, the amino-undecanoic acid 11 is obtained: this is the Rilsan® polyamide 11 monomer
- Rilsan® PA11 (Arkema) is used in a large number of applications thanks to its outstanding properties: excellent resistance to chemicals (particularly hydrocarbons), ease of processing, a wide range of working temperatures (-40°C / +130°C), high dimensional stability and low density.
- Applications: tubing, fuel lines, hydraulic hoses.

Polyamide 6.10

- When castor oil is added slowly to an 80% caustic solution, the sodium ricinoleate formed splits to form sodium sebacate and capryl alcohol.
- Sebacic acid is condensed with hexamethylene diamine to form nylon 6,10.
- In 2007 BASF launched a polyamide 6.10 called Ultramid BALANCE based to the extent of about 60% on sebacic acid (decanedioic acid) derived from castor oil.
- Ultramid Balance combines a relatively low density for a polyamide with good low-temperature impact resistance and great dimensional stability due to its low water absorption.
- Accordingly, it can be employed not only in classic PA 6 applications, but also wherever the use of PA 6 in the past has run up against limitations

http://corporate.basf.com

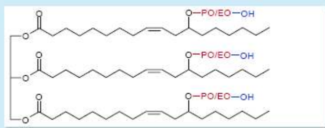
Castor oil based polyurethane

- BASF Lupranol BALANCE: polyols on the basis of renewable raw materials: castor oil
- The triglyceride of ricinoleic acid from castor oil has the same functionality - three hydroxyl groups per molecule - as the initial raw materials currently used for flexible foam production.
- It can replace conventional polyols directly without a change to the formulation.
- **Mattresses made up of almost 25% renewable raw material** The new product is made up of 31% castor oil. A finished mattress made with Lupranol® BALANCE contains up to 24% by weight of castor oil, without impairing the performance of the foam.

Synthesis with DMC (BASF patent)

Castor oil

DMC

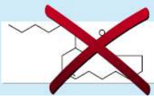


Polyetherol

Catalytic polyaddition of propylene and/or ethylene oxide

DMC: Double-metal cyanide catalysis

- Neutral
  - ➔ No saponification
  - ➔ No formation of the ring of ricinoleic acid
  - ➔ Low in odors



Odor!

- At 3.8 million metric tons, flexible foams make up a high percentage of the worldwide polyurethane consumption.
- The areas of application include the furniture and mattress industries, which account for over 80%.
- It can also be used in technical applications such as textile lamination or in automotive construction.

BASF Lupranol BALANCE

Biobased epoxy

- Biobased epoxy materials can be prepared from diglycidyl ether of bisphenol A (DGEBA) and epoxidized castor oil (ECO)
- As a result, the thermal stability of the cured epoxy blends showed a maximum value in the presence of 10 wt.-% ECO content, which was attributed to the excellent network structure in the DGEBA/ECO blends.
- The storage modulus and glass transition temperature of the blends were lower than those of neat epoxy resins.
- The mechanical interfacial properties of the cured specimens were significantly increased with increasing the ECO content.
- The addition of larger soft segments of ECO into the epoxy resins reduces the crosslinking density of the epoxy network, which results in increasing toughness in the blends.

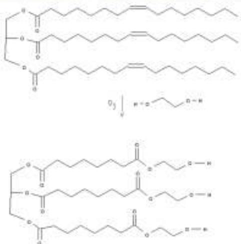
PARK Soo-Jin [(1)] ; JIN Fan-Long [(1)] ; LEE Jae-Rock [(1)] ; Macromolecular chemistry and physics , 2004

Other vegetable oils

- Other vegetable oils - such as soy bean oil, peanut oil, and canola oil - contain carbon-carbon double bonds, but no hydroxyl groups. There are several processes used to introduce hydroxyl groups onto the carbon chain of the fatty acids, and most of these involve oxidation of the C-C double bond (ozonolysis).

Soy bean

Canola



Triolein with ozone and ethylene glycol.

Soy based polyurethane

- Just over 2.1 pounds of CO_2 are removed from the atmosphere when producing one pound of soy polyol.
- Producing 1 pound of petroleum based polyol adds 3.59 pounds of CO_2 to the atmosphere.
- Therefore, if 1 pound of petroleum polyol is replaced with 1 pound of soy polyol, a total of approximately 5.6 pounds of CO_2 will be removed from the atmosphere.
- Applications:
  - Coatings, Adhesives, Sealants, & Elastomers
  - Flexible Molded Foam
  - Rigid Molded Foam
  - Slabstock
  - Spray Foam Insulation

Spray Foam Insulation

Insulated foam cup made with Agrol®

Automotive application
A far better use for soy than tofu

- Ford intends to replace 40 percent of the standard petroleum-based polyol with a soy-derived material.
- Most automotive manufacturers today use a 100 percent petroleum-based polyol foam.
- Per year, the U.S. market for this material is 3 billion pounds - 9 billion pounds worldwide.
- An average of 30 pounds of petroleum-based foam is used in each vehicle produced.
- The reduced need for petroleum-based products is one advantage; the reduced CO2 emissions, up to 24 percent renewable content and lower energy needed to produce the material.

2008 Ford Mustang - http://www.edmunds.com/

Biobased rigid polyurethane

- Corn and soy beans are being used to develop bio-based and soy-based **polyols** for composite polyurethanes.
- Bayer MaterialScience has a long history in this area: in 1999, Bayer MaterialScience developed a soy-based rigid polyurethane RIM system for John Deere to create long-lasting, strong, yet flexible, composite panels for the construction of their combines (Baydur 730S IBS).

Green Houses

- Biobased polyurethane for building products allows residential and commercial structures to be more sustainable, making it is more energy efficient and healthier than traditionally insulated homes.

http://www.aia.org/aiarchitect/

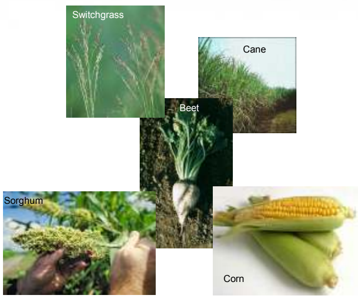
Soy based epoxy

- A potentially inexpensive alternative epoxy resin system based on soybean oil has been developed for polymer composite applications.
- Epoxidized methyl soyate (EMS) and epoxidized allyl soyate (EAS) have been synthesized at the University of Missouri-Rolla.
- These materials consist of mixtures of epoxidized fatty acid esters.
- The epoxidized soy-based resins provide better intermolecular crosslinking and yield materials that are stronger than materials obtained with commercially available epoxidized soybean oil (ESO).
- Soy based epoxy resin may be used as low cost and biocompatible coating materials for food and beverage cans.

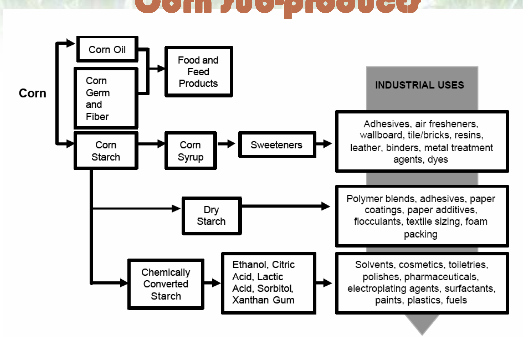
JIANG ZHU; CHANDRASHEKHARA K.; FLANIGAN Virgil ; KAPILA Shubhender Journal of applied polymer science, 2004, vol. 91, n°6, pp. 3513-3518

Sugar based polymers

- Glucose is produced commercially via the enzymatic hydrolysis of starch.
- Many crops can be used as the source of starch.
- Maize, rice, wheat, potato, cassava, arrowroot, sorghum, switchgrass and sago are all used in various parts of the world.



Corn sub-products



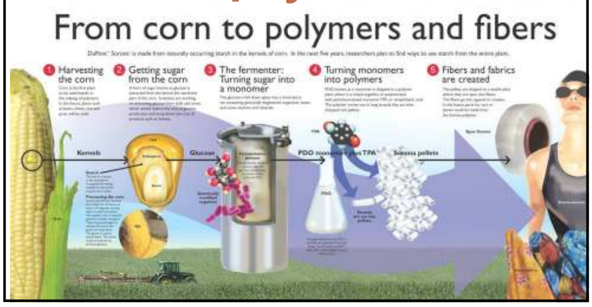
Ralph W. Pike

http://www.mpri.lsu.edu/Integrating_Biomass_Feedstocks_into_Chemical_Production_Complexe

Du Pont's Sorona renewable source polyester fibers

• 30% to 37% renewably sourced polyester derived from corn sugar propanediol (PDO).
• Sorona® EP thermoplastic polymer resins are polytrimethylene terephthalate resins made from Bio-PDO, which is derived from corn.

Du Pont's Sorona renewable source polyester fibers

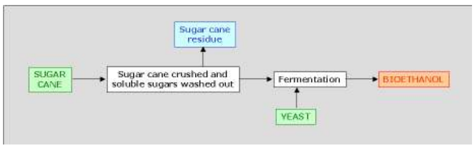


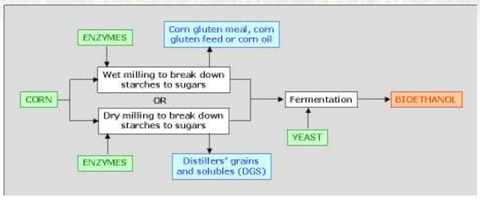
Ethanol production

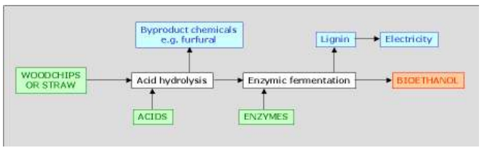
- Bio-ethanol is produced by yeast fermentation:

$$C_6H_{12}O_6 \rightarrow 2\ CH_3CH_2OH + 2\ CO_2$$

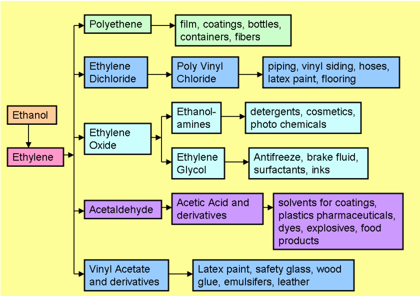
- In order to produce ethanol from starchy materials such as cereal grains, the starch must first be converted into sugars. Biomass and cellulose can also used.







Ethanol based polymers and chemicals



Ralph W. Pike

http://www.mpri.lsu.edu/Integrating_Biomass_Feedstocks_into_Chemical_Production_Complexe

Green Polyethylene

- Ethanol is readily converted to ethylene in a process that uses an activated alumina catalyst in a fluidized bed at 300°C with a 99% conversion.
- Dow Chemical and Crystalsev, a Brazilian sugar and ethanol producer, plan to build a 300,000 m.t./yr ethylene plant in Brazil to manufacture 350,000 m.t./yr of low density polyethylene from ethanol.
- Braskem, a Brazilian petrochemical company, plans to produce 200,000 m.t./yr of high density polyethylene from sugar (C&E News, 2007b).
- Solvay's South American affiliate plans to build a plant in Santo Andre, Brazil, to produce 60,000 tons per year of sugar cane derived ethylene which will be combined with chlorine to produce poly vinyl chloride plastic (PVC) (C&E News, 2007c).

Green Polyethylene

Braskem Produces First Ethanol-Derived Polyethylene

23 June 2007

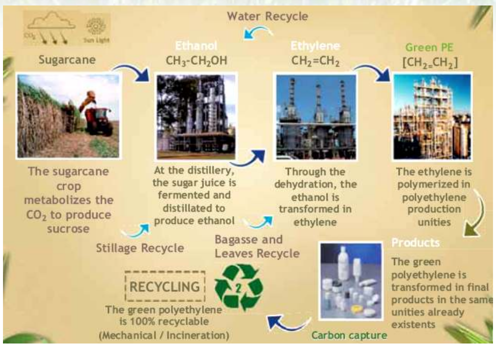
Brazil's Braskem has produced its first polyethylene made from sugarcane ethanol. The polymer was certified to contain 100% renewable raw materials.

The project is now in technical and economic specification process and the startup of green polyethylene production on an industrial scale is expected in late 2009. The new unit will have modern technology and competitive scale, and could reach annual production capacity of up to 200,000 tonnes. The location and industrial design of the unit will be determined within the next few months.

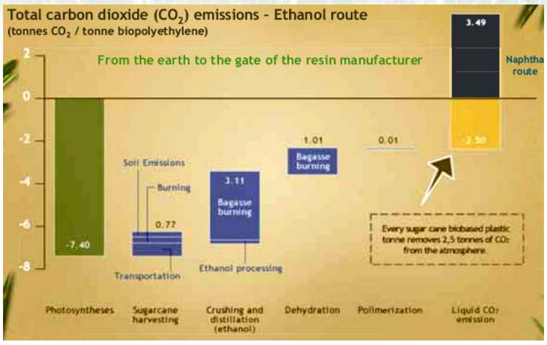
Braskem is Latin America's leading company in the thermoplastic resins segment in Latin America and second largest Brazilian industrial company owned by the private sector. International laboratory Beta Analytic certified the product.

The polymer developed by Braskem—a high-density polyethylene, one of the resins most widely used in flexible packagings—is the result of a research and development project that has already received some US$5 million in investment.

Part of this amount was allocated to implementing a pilot unit for the production of ethane, which is the basis for the production of polyethylene, from renewable feedstock at the Braskem Technology and Innovation Center.



www.braskem.com



www.braskem.com

Braskem extends bioplastics range with LLDPE

28.03.2008

- New bio-based route to produce butene will allow the development of a bio-derived LLDPE for applications in flexible film packaging.
- Braskem has the advantage over its rivals in the bioplastics sector of Brazil's well established sugar cane ethanol industry.
- The country is the world's largest producer of sugar cane bioethanol.
- Braskem claimed that its route to bio-HDPE had the potential to cost less than current petrochemical technology.
- However, pricing will initially be determined by the value in the market rather than cost to manufacture.
- The company has made no comment on the cost of its bio-butene or LLDPE products.

What's next?

Microalgal Biopolymers

- Microalgae are microscopic algae, typically found in freshwater and marine systems.
- Algal oils posses characteristics similar to those offish and vegetable oils, and can thus be considered as potential substitutes for the products of fossil oil
- Fermentation of algal biomass can produce either methane or ethanol.
- Lipid content can be enhanced, 70 to 85% on a dry weight basis were reported in microalgae.
- Microalgae can assimilate CO_2 gas as a carbon source for growth.
- Bioplastics can be synthesized by microalgae.

Summary and conclusions

- Main benefits of durable bioplastics: CO_2 emission reduction and saving fossil resources.
- High consumer acceptance.
- Recycling options can be used.
- High market potential.
- New opportunities for 3rd world countries as bioplastics raw material producers