• Designing of Environmentally Safe Marine Antifoulant:

Fouling of the underwater area of ships with algae, other micro-organisms and small invertebrates has a serious impact on the operational costs of shipping due to increased fuel consumption and may lead to the introduction of non-endemic species in sensitive environments. Biocide based antifouling paints are widely used to prevent fouling. Since the mid-1960s **TBT** or **Tributyltin** has been applied in most antifouling paint systems because of its brilliant antifouling properties over ship's hull as it prevents the growth of algae, barnacles and other marine organisms. Due to strong eco-toxicity of TBT, serious effects observed in oyster cultures, costal mollusk populations and some deep water snail species, many countries have banned the application of TBT based paints.

After the TBT era: Alternative anti-fouling paints and their ecological risks:

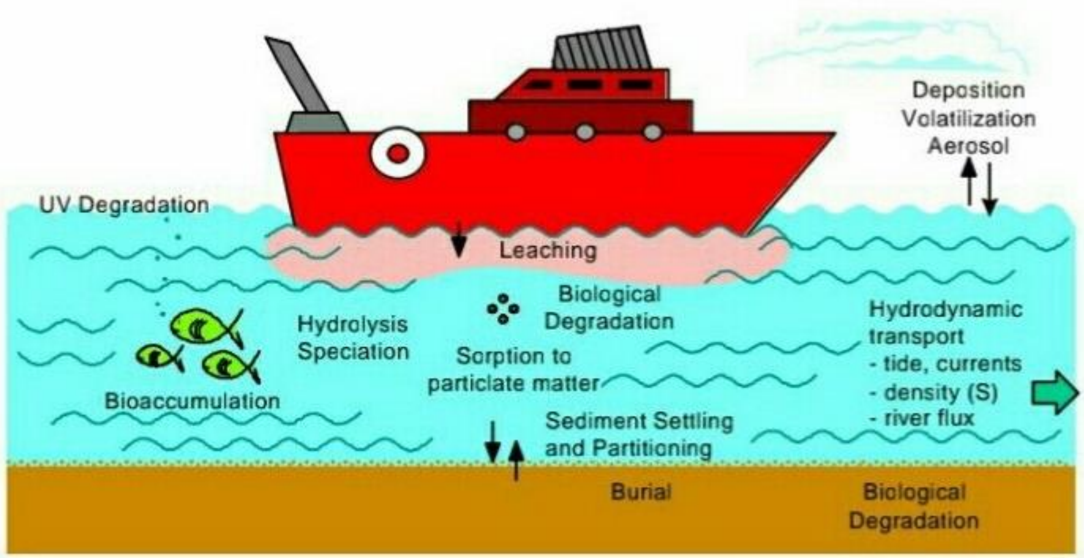
During 1998 the Marine Environmental Protection Committee of the International Marine Organization (IMO MEPC-42) adopted a resolution, aiming at further restrictions of TBT on large ships in 2003 (end of application) and 2008 (expected implementation of ban). It is expected that in the coming decade many new products will enter the market. Although substituents are already on the market, research efforts for novel antifouling technologies are intensified. Since that period various new paints, usually based on high loading copper in combination with organic biocide, have been applied in the pleasure boating sector. Biocide is a chemical substance or microorganism exert a controlling effect on any harmful organism by chemical or biological means. Biocide free coatings are being used on a limited scale or still in the testing phase.

In current assessment procedures, antifouling agents are treated in a very generic way. Predicted environmental concentrations are derived with generic multimedia models which do not account for the complex hydrodynamic processes in the marine environment.

Environmental fate of Antifouling products:

Many complex and interacting processes that can be of a biological, chemical or physical nature, determine the chemical fate of contaminants in the marine environment. Some of major transport and transformation processes have been summarized in the following figure and following table. For compounds with a high affinity to particulate matter or sediment, sedimental transport phenomena will be of dominant importance. Stable dissolved compounds are likely to be affected most by river discharges or tidal currents. In specific marine environments with low exchange rates or pseudo stagnant conditions the chemical and biological processes will become more important.

Chemical fate processes of antifouling products in the marine environment



Transport and transformation processes determining the fate of chemical compounds in produced water. (Adapted from Miller, 1982, Mackay 1991).

	Transport	Transformation
Abiotic	*Physical processes*	*Chemical processes*
	Hydrodynamical transport	Hydrolysis
	Dispersion, diffusion	Photolysis
	Dissolution	Photo-oxidation
	Emulsification	Polymerization
	Precipitation	Complexation, speciation
	Sorption to particulate matter	Dissociation
	Sorption to dissolved org. matter	Oxidation
	Sedimentation	Reduction
	Resuspension	
	Burial	
	Volatilisation	
	Accumulation in microsurface layer	
	Aerosol formation	
	Atmospheric deposition (wet / dry)	
Biotic	*Biological processes*	*Biochemical processes*
	Uptake, elimination	Biodegradation in water (aerobic)
	Bioconcentration, bioaccumulation	Biodegradation in sediment (anaer.)
	Excretion of biotransf. Products	Biochemical processes
	Food chain transfer	Biotransformation
	Bioturbation	(Detoxification, hypertoxification)

There is a broad distinction between organic and inorganic compounds both in the mechanisms and relative importance of the processes. For instance, for copper, processes such as adsorption, sedimentation, redox reactions have a prominent role in the fraction of freely bioavailable and potentially toxic Cu^{+2}. Among the trace elements mechanisms, partitioning and rate constants are highly element specific and may depend strongly on the physico chemical specification. The specification is highly dependent on environmental factors such as salinity, pH, particulate matter, presence and nature of ligand-substrates.

Emission patterns of Antifoulants:

Emissions of antifouling products cannot easily be estimated. Usually the emissions are quantified as the product of a leaching rate ($\mu g/cm^2$/day) and the total antifouled underwater area. The leaching rate depends on the type of compound, characteristics and age of paint matrix and velocity of the ship. The total antifouled underwater area depends on shipping intensities, dimensions of the various categories of ships, and many other factors such as cargo load and residence time of the various ships.

In a recent report of the CEPE Antifouling Working Group (CEPE AWG, 1998) a classification has been made of the various classes of biocidal antifouling coatings. The following types of coatings were identified: soluble matrix; insoluble matrix, TBT self-polishing copolymer and TBT free self-polishing antifoulings.

Both the soluble and insoluble matrix types contain copper oxide as the main biocide, with specific additional biocides (sometimes referred to as 'boosters') to prevent fouling from copper resistant fouling species. With typical in-service periods of 12-18 months, the biocide-release rate decreases exponentially during the lifetime of the coating. After the in-service period the release rate drops below the critical level needed to prevent fouling.

Both the TBT self-polishing copolymers and TBT free self-polishing paints, which both may contain copper, have a different biocide release pattern. The biocide release rate shows a rapid decrease in the first months to year, followed by constant release rate during the remaining in-service period of up to 5 years. The velocity of the ship has a strong impact on the leaching rate.

Leaching rate estimates used in a brief selection of recent experimental or risk assessment studies have been summarized in the following table. For each compound a broad range of leaching rate estimates is observed. Copper leaching rates usually are higher than for other compounds. Leaching rates reported for TBT usually are below regulatory implied values of 4 μg/cm2/day in some countries (USA, Sweden).

Summary of leaching rate estimates reported from various studies

Compound	Leaching rate $\mu g/cm^2/day$	Type of study	Author
TBT	4	North Sea	Stronkhorst *et al.* (1996)
	2.5	Marina	Johnson and Luttik (1996)
	0.1 – 5	Harbour	Willingham and Jacobson (1996)
	1.3 – 3.0	Ships > 25m	Lindgren *et al.* (1998)
Cu	6.2	Marina	Matthiesen and Reed (1997)
	1-20	Not specified	Hare (1993)
	8 – 25	Ships >12m	Lindgren et al. (1998)
	37 – 101	Ships > 25m	Lindgren *et al.* (1998)
	4 – 6 *	Exp. Studies	Berg (1995)
Irgarol	2 – 16	Marina	Ciba (1995)
	5	Marina	Scarlett *et al.* (1997)
	2.5 – 5	Exp. Studies	Thomas et al. (1999)
Sea-Nine 211	1 (0.1 – 5)	Harbour	Willingham and Jacobson (1996)
Zinc Omadine	3.3	Exp. Studies	Thomas et al. (1999)
Diuron	0.8 – 3.3	Exp. Studies	Thomas et al. (1999)
Dichlofluanid	0.6 – 1.7	Exp. Studies	Thomas et al. (1999)

* after 21 days. During the first 21 days leaching rates ranged between 7 – 61 $\mu g/cm^2/day$.

• An efficient green synthesis of a compostable and widely applicable plastic (poly lactic acid) made from corn:

Poly (Lactic Acid): Green and Sustainable Plastics:

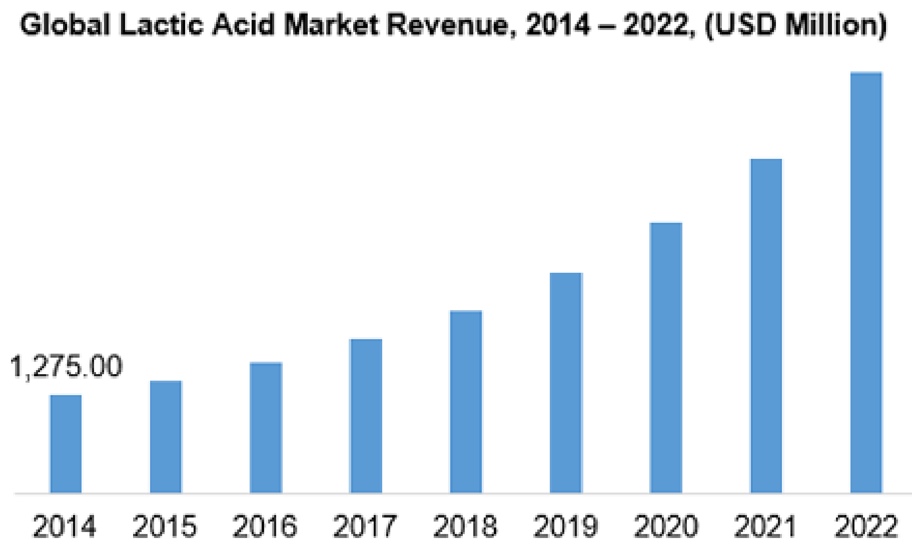
Management of solid waste consists of polymeric materials from petrochemical resources such as thermoplastics (e.g. products of polyethylene terephthalate, polypropylene and polyethylene) and thermosets (e.g. products of synthetic rubbers, phenolic and epoxy resins) is an important worldwide problem. There are high capital and operating costs as well as environmental pollution problems associated with incineration. Used dumped polymeric materials such as plastic bottles and containers, tyres and electric switches have slow or nominal degradation in the landfill. The landfills are limited and dumped polymeric materials contain toxic materials such as lead and cadmium which were used as colorants, stabilizers and plasticizers during their production. These toxic materials may leach to the soil and impose serious environmental risk. Moreover, petrochemical resources are progressively diminishing and the oil prices are radically increasing. All of these issues add with increasing consumer interest in sustainable green products and have sparked research and development in favor of biodegradable polymeric materials from renewable resources.

Amount of energy required from non-renewable sources and CO_2 emissions for different types of plastics currently on the market.

Type of plastic	Energy requirement, MJ/kg	Global warming, kg CO_2 eq/kg
From non-renewable sources		
HDPE	80.0	4.84
LDPE	80.6	5.04
Nylon 6	120.0	7.64
PET	77.0	4.93
PS	87.0	5.98
PVOH	102.0	2.70
PCL	83.0	3.10
From renewable sources		
TPS	25.4	1.14
TPS + 15% PVOH	24.9	1.73
TPS + 60% PCL	52.3	3.60
PLA	57.0	3.84
PHA	57.0	Not Available

Poly lactic acid (PLA) is one of the most versatile environment friendly biodegradable thermoplastic polyester. It is linear aliphatic thermoplastic polyester derived from 100% green and renewable sources such as **corn**, **sugarcane** and **rice**. PLA is produced from lactic acid (LA) monomer. LA monomer was approved as food additive. This makes PLA a unique **green polymer** that has low toxicity in addition to comparable performance to petroleum-based plastics. PLA has wide range of properties such as bio-compatibility, bio-degradability, less toxicity, vast range of mechanical properties and the ability to be molded into different shapes. These properties make it a very suitable material for applications similar to plastics and more widely in biomedical fields. Various research and studies are being carried out around the world on PLA and PLA has proved itself to be very promising material in field of bone fixation, drug delivery vehicle, tissue engineering and various other biomedical applications. Besides being biodegradable and having produced from renewable resources, PLA provides numerous other benefits including: fixation of carbon dioxide, a greenhouse gas, significant amount of energy savings, improvement of farm economies and manipulation of physico-mechanical properties using polymer architecture such as orientation, blending, branching, cross-linking and plasticization. All of these properties make it a polymer of choice for biomedical (e.g. implants, sutures, drug encapsulation), food packaging (e.g. food wrap, container, drinking cups) and structural applications (e.g. civil structures, furniture, marine, automobiles).

Low molecular weight PLA was produced by Carother et al. in 1932. The development in the field of PLA first started in 1983 with publication of production formulas of lactide by Bichoff and Walden. A Japanese industry, Shimadzu Corporation and Kanebo Goshen Ltd. Started commercial production of PLA in 1994 by fiber and melt spinning and sold it under trade name lactron. France started producing PLA under trade name Deposa in 1997. Cargill and Dow were first to produce PLA in large scale in USA under joint venture named Nature Work LLC. In 2009 nature work was completely owned by Cargill. At present time, many countries like Switzerland, China, and Korea are taking initiative in the production of PLA.

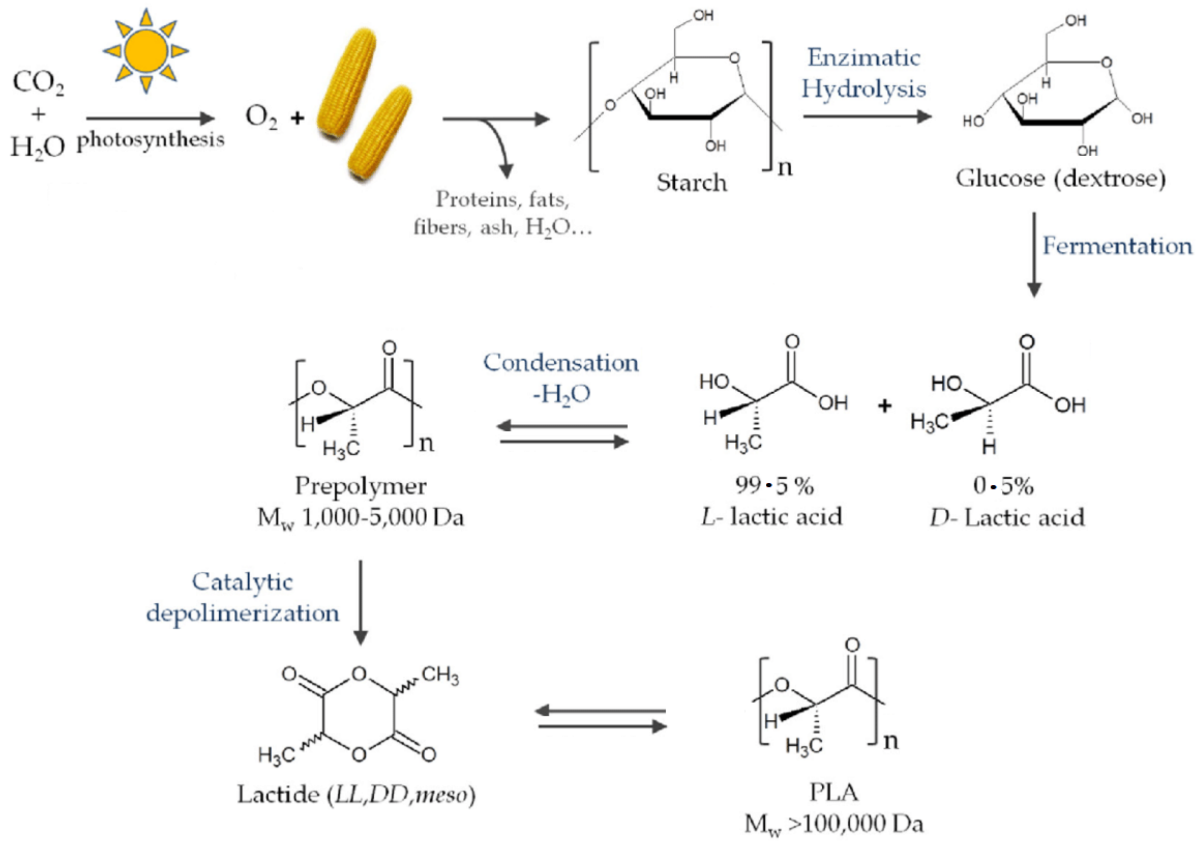


POLYLACTIDE: SOURCES AND SYNTHETIC ROUTES OF PRODUCTION

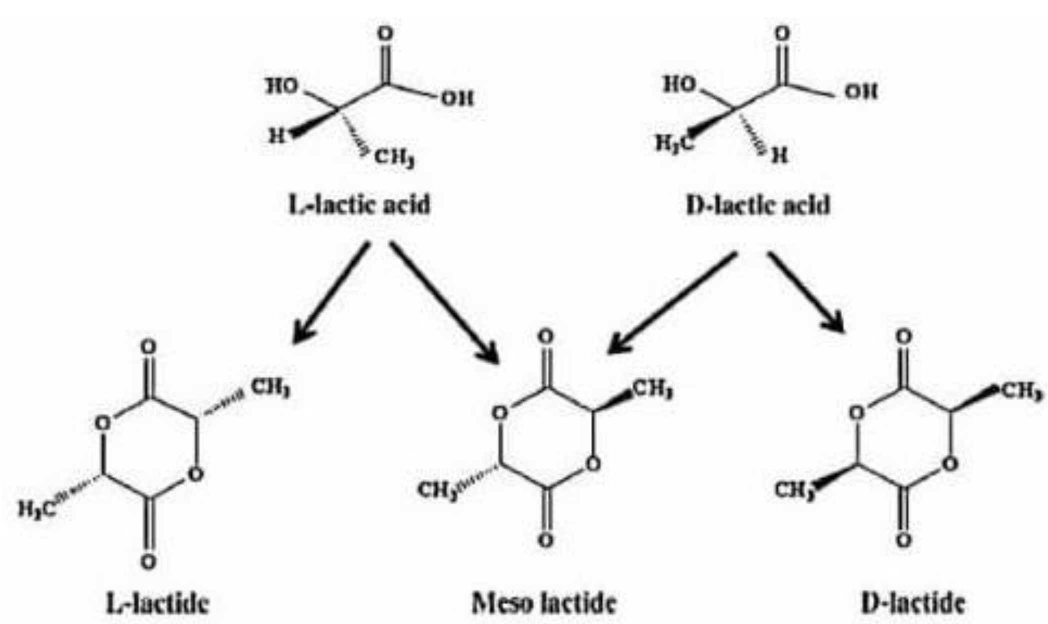
Synthesis of PLA can be obtained generally by two routes, namely (i) direct condensation of lactic acid and (ii) ring-opening polymerization (ROP) of lactide (a cyclic dimmer of lactic acid) as shown in the following figure.

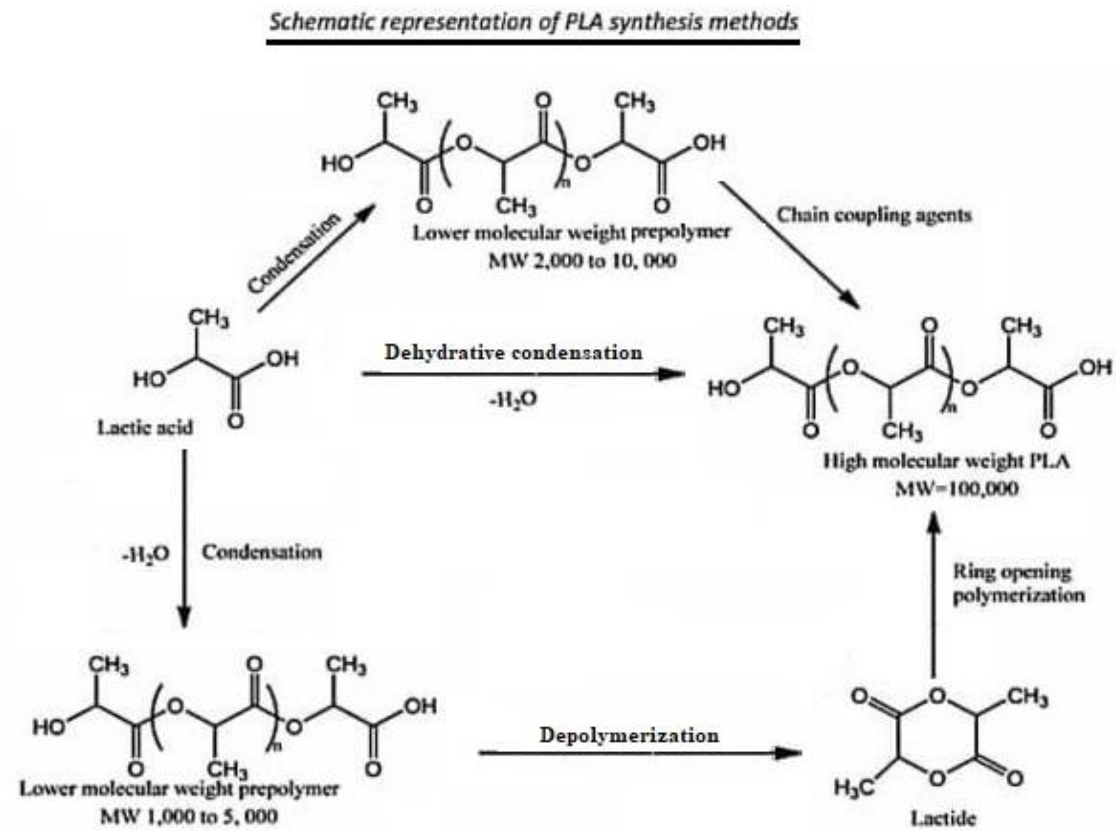
PLA produced by direct condensation of lactic acid is a brittle (or breakable or fragile) polymer and generally unusable. This polymerization technique has some other drawbacks including need for large reactor, evaporation, solvent recovery and increased racemization.

In ROP route, either D-lactic acid, L-lactic acid, or a mixture of the two are prepolymerized to obtain an intermediate low molecular weight poly lactic acid, which is then depolymerized into a mixture of lactide stereoisomers. Lactide is generally formed by the condensation of two lactic acid molecules as follows: L-lactide from two L-lactic acid molecules, D-lactide from two D-lactic acid molecules, and meso-lactide from one L-lactic acid and one D-lactic acid molecule. After purification the lactides are polymerized into high molecular weight PLA.

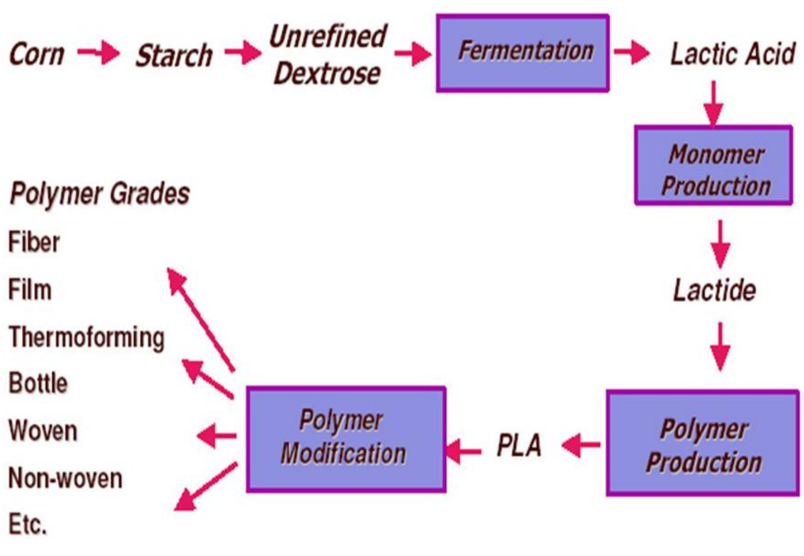


: Different Stereoforms of Lactide :



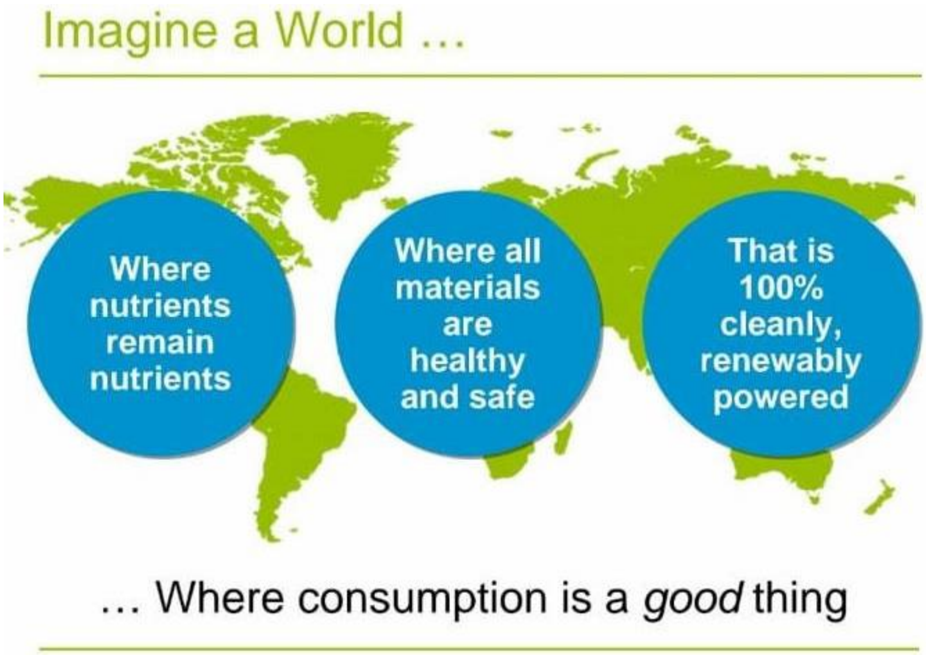


Poly lactic acid (PLA) for plastics production



In the USA, corn is the cheapest starch-rich and most widely available annually renewable resource from which lactic acid is produced. In other parts of the world, locally available crops such as rice, cottonseed hull, grapefruit, sugar beets, sugarcane, wheat and sweet potatoes can be used as a starch/sugar feedstock.

- # Development of fully Recyclable Carpet: Cradle to Cradle Carpeting:



Imagine a world where existing products and buildings are not thrown away but are kept in use, renewed where necessary. This could not only reduce demand for new raw materials and energy but could also lead to zero waste.

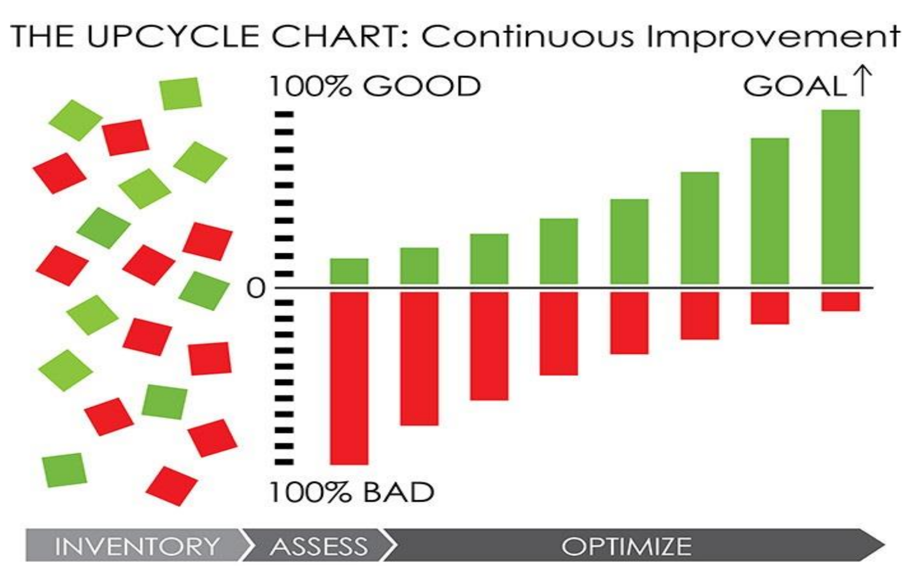
Cradle to cradle design (also referred to as C2C) is a biomimetic approach to the design of products and systems that models human industry on nature's processes, where materials are viewed as nutrients circulating in healthy, safe metabolisms. C2C suggests that industry must protect and enrich ecosystems and nature's biological metabolism while also maintaining a safe, productive technical metabolism for the high quality use and circulation of organic and technical nutrients. It is a holistic, economic, industrial and social framework that seeks to create systems that are not only efficient but also essentially waste free.

In the cradle to cradle model, all materials used in industrial or commercial processes such as metals, fibers, dyes- fall into one of two categories: "technical" or "biological" nutrients.

- **Technical nutrients** are strictly limited to non-toxic, non-harmful synthetic materials that have no negative effects on the natural environment, they can be used in continuous cycles as the same product without losing their integrity or quality. In this manner these materials can be used over and over again instead of being *"downcycled"* into lesser products, ultimately becoming waste.

Downcycling is the reuse of materials into lesser products. For example, a plastic computer case could be downcycled into a plastic cup, which then becomes a park bench, etc., this eventually leads to plastic waste. In conventional understanding, there is no difference from recycling that produces a supply of the same product or material.

- **Biological nutrients** are organic materials that once used, can be disposed of in any natural environment and decompose into the soil, providing food for small life forms without affecting the natural environment. This is dependent on the ecology of the region. For example, organic material from one country or landmass may be harmful to the ecology of another country or landmass.



Initially defined by McDonough and Braungart, the Cradle to Cradle Products Innovation Institute's five certification criteria are:

- **Healthy materials**, which involves identifying the chemical compositions of the materials that make up the product. Particularly hazardous materials (e.g. heavy metals, pigments, halogen compounds etc.) have to be reported whatever the concentration and other materials reported where they exceed 100 ppm. The risk (hazard) for each material is assessed against criteria and eventually ranked on a scale as follows:
  - ***Green*** - being materials of low risk
  - ***Yellow*** - being those with moderate risk but are acceptable to continue to use,
  - ***Red*** - materials that have high risk and need to be phased out
  - ***Black*** - banned materials because of extreme hazards
  - ***Grey*** - materials with incomplete data.

- **Material reutilization**, which is about recovery and recycling at the end of product life.

- **Water efficiency**, particularly usage and discharge quality.

- **Energy efficiency,** assessment of energy required for production, which for the highest level of certification needs to be based on at least 50% renewable energy for all parts and subassemblies.

- **Social responsibility**, which assesses fair labor practices.

The certification is available at several levels: basic, bronze, silver, gold, platinum, with more stringent requirements at each.

CERTIFIED cradletocradle CM — BRONZE

CRADLE TO CRADLE CERTIFIED[CM] PRODUCT SCORECARD

QUALITY CATEGORY	BASIC	BRONZE	SILVER	GOLD	PLATINUM
MATERIAL HEALTH				✓	
MATERIAL REUTILIZATION			✓		
RENEWABLE ENERGY & CARBON MANAGEMENT		✓			
WATER STEWARDSHIP			✓		
SOCIAL FAIRNESS				✓	
OVERALL CERTIFICATION LEVEL		✓			

EXAMPLE:

CLIMATEX biodegradable seat cover fabrics

CERTIFIED cradletocradle CM — GOLD

- Materials positively defined as biological nutrients
- Ecologically safe dye chemicals
- Lowering overall production costs
- Fully biodegradable and compostable
- Factory water output cleaner than input

- Eliminating need of filtering dyes and chemicals
- Trimmings no longer toxic
- Proactive approach toward increasing regulative pressure

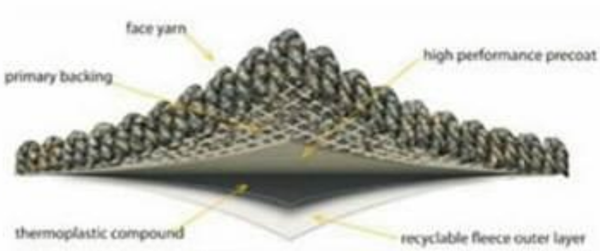
Steelcase: Think Chair

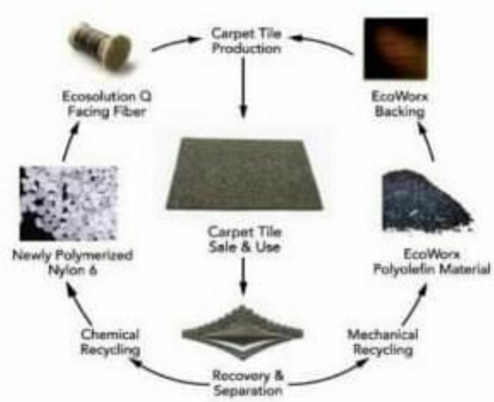
- Highly recyclable (99% by weight)
- Disassembly in 5 minutes using common hand tools
- Customers actively invited to participate in recovery
- Up to 44% recycled content
- Green-guard indoor air quality certified
- Reducing fatigue and discomfort by adopting to the way you sit

- Original iconic design
- Environmentally sound
- profitable
- TPU instead of PVC (energy footprint)
- Producing renewable (wind)energy

Shaw Carpet Tiles

- PVC-free, fully recyclable
- Designed to be remanufactured, again and again
- In a continuous loop (carpet to carpet)
- Up-cycling 121 million pounds of carpet waste yearly
- 100+% take back,
- Increased profitability & turn-over






ECOWORX® TILE BACKING
100% PVC and Phthalates free
Contains 44% recycled content
40% lighter than PVC alternatives
Supported by environmental guarantee that provides free cradle-to-cradle recycling


ECO SOLUTION Q®
PREMIUM BRANDED NYLON
Commercial fiber of choice because it is tough, resilient, beautiful and fully recyclable.
Available in over 200 color options
Extensive Performance Warranties
Contains 25% post consumer and 20% pre-consumer recycled content

EVERGREEN NYLON RECYCLING

- **100 million pounds** of post-consumer Nylon 6 carpet fiber is recycled every year through Evergreen
- **31%** life cycle energy savings as compared to virgin Caprolactam

MORE EXAMPLES

- Eating utensils made out of non-toxic, organic, completely biodegradable materials that "you can feel good about throwing away" (instead of guilty)
- Shoes made out of 2 parts: Sole of rubber ("technical nutrient") and upper of biodegradeable material ("biological nutrient") that you rent instead of buy; when it is worn out, you return it to the manufacturer, who disposes of upper and reuses sole