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Biodegradable Plastics - The Concept and Options

Since the discovery of man-made polymers continuous and systematic efforts have been made to make polymers more stable, mechanically stronger and chemically and environmentally durable. Rot-resistance and rust proof are the two important factors for the large-scale popularity and demand of synthetic polymers. Now the use of synthetic polymers, due to their low price, ready availability, wide spectrum colorability, and ease of fabrication in any desired shape has been accelerated to such an extent particularly in the affluent countries, that the disposal of the used products has become increasingly difficult. Besides, there are certain end-uses where a limited lifetime of the plastics products is desirable.

The degradation of this discarded/disposed off polymer waste has become a challenging task. Though recycling of these disposed off polymers is a widely accepted option, still for some low life span plastics, quick degradation may be a desirable phenomenon from the waste management point of view.

At this stage, the necessity of developing degradable commodity polymers was felt. Polymers, which were initially developed to withstand the mechanical and environmental abuse during its useful life are required to be degraded immediately after their intended life span. This is a greater challenge.

Polymers can be degraded by three principal agents viz. (a) light or high-energy radiation, (b) heat and oxygen (c) microbes.

Degradation of a polymer by light, known as photo-degradation, is initiated first by the absorption of light energy by the appropriate group present in the polymer molecule. The

initial act of light absorption results in the scission of the polymer molecule at an appropriate position of the chain leading to smaller fragments (Fig.1). These fragments are either eventually mix with dust or the smaller volatile fragments escape to atmosphere. So photo-degradable polymers require either an in-built photo responsive group in the chain or an additive.

Degradation of polymer by heat energy generally receives support from oxygen of the atmosphere and is, therefore, known as thermo-oxidative degradation. The primary act in this process is the rupture of bonds of the macromolecules resulting in radical sites. These radical sites react with oxygen present in air to form peroxy radicals. Thus, again the long chain polymer molecules are converted into smaller fragments and volatiles (Fig 1).

However, biodegradation follows a different path. Since most of the synthetic polymers are resistant to microbial attack, biodegradation of polymers may be achieved by two major paths, viz. (a) design of a polymer from monomers which are vulnerable to micro-organisms, and (b) incorporation of biodegradable additive or groups in the polymer.

Fig. 1:

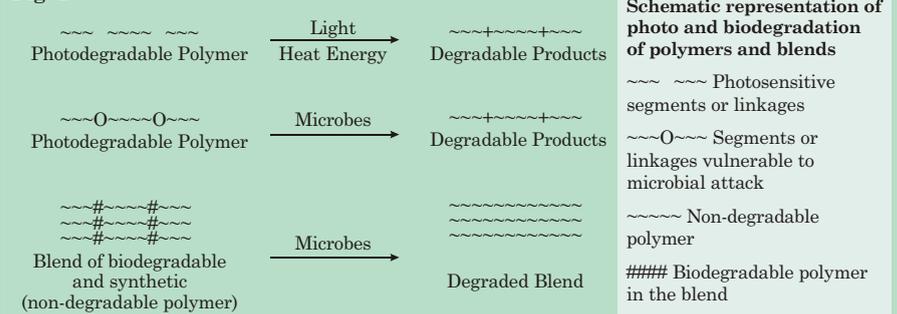
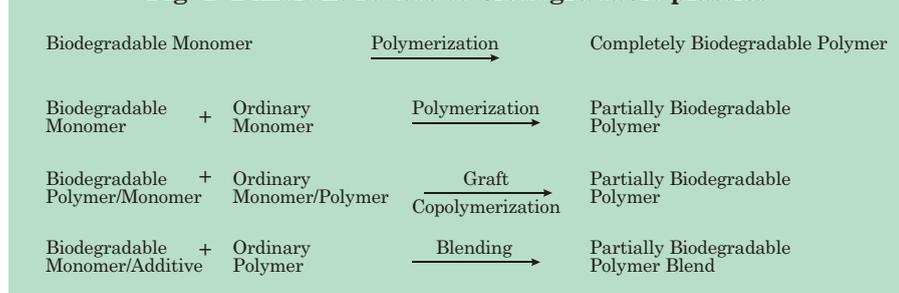


Fig. 2: Different routes to biodegradable plastics



process technology for partial biodegradable plastics either by incorporating a biodegradable additive as a masterbatch, or by blending a biodegradable natural polymer with industrial polymers appears to be successful. The choice of starch for development of biodegradable plastics is dictated by the following factors:

This, in turn, can be done by two methods. The first one involves the copolymerization of biodegradable monomer/polymer with the non-degradable monomer/polymer, and the second method involves the blending of a biodegradable additive/polymer with a non-degradable polymer (Fig.2). Polymers obtained from biodegradable monomers such as poly-l-lactic acid or poly-hydroxybutyrate are completely biodegradable (Fig 3). On the other hand, the second group of biodegradable polymers is only partially biodegradable and is in fact converted into smaller fragments to be mixed with dust (Fig. 1). Comparative study of these three routes to polymer degradation is presented in Table 1.

Starch is cheap, abundantly available, renewable, non-toxic, readily attacked by microbial agents, and has reactive groups to form various derivatives for its modification of properties. Therefore, currently most of the commercial processes for biodegradable plastics are based on incorporating starch or its derivatives to olefin polymers (Table 2). Olefin polymers are the largest volume commodity polymers today for their low cost, abundant supply of feedstocks and good overall performance.

Table 1 : Various Polymer Degradation Routes

	Photo-degradation	Thermo-oxidative degradation	Biodegradation
Active Agent	UV light or high energy radiation	Heat and Oxygen	Microbial agents
Requirement of heat	Not required	Higher than ambient temperature required	Not required
Rate of degradation	Initiation is slow. But propagation is fast	Fast	Moderate
Other consideration	Environment friendly if high energy radiation is not used	Environmentally not acceptable	Environment friendly
Overall acceptance	Acceptable but costly	Not acceptable	Cheap and very much acceptable

Three general technologies are now available to manufacture starch-based olefin biodegradable plastics:

- Modification of starch and incorporation of modified starch into olefin polymers.
- Modification of olefin polymers and incorporation of starch into modified olefin polymers, and
- Blending of starch and olefin polymers in presence of a coupling agent.

A list of early manufacturers of biodegradable plastics is shown in Table 3

(From Summary Note of a Project on development of Biodegradable Plastics - by IPCL & IIT, Kharagpur - 1999)

Process Technology for Biodegradable Plastics

Development of process technology for completely biodegradable polymers is generally costly. Either the cost of monomers is prohibitive for its commercialization, or the polymerization technology is not yet competitive with the conventional processes. Further research and development efforts are necessary to make the biotechnological routes to biodegradable polymers cost effective. However, in special cases such as biodegradable polymers for medical applications these processes may be viable.

Another drawback to the development of completely biodegradable polymers is the limited availability of monomers. For industrial polymers a large variety of monomers and feedstocks is available. Consequently the properties offered by completely biodegradable polymers are limited and, therefore, they could not replace the industrial non-degradable polymers.

Since most of the biodegradable plastics are for disposable terms their cost of production is the determinant factor for commercialization. Thus the

Table 2 : Polymers and Additives used for biodegradable plastics

Polymers	Additives
Polyethylene (LDPE, LDPE + LLDPE, HDPE)	Starch, modified starch, EAA, EVA, NH ₄ OH etc.
Hydrolyzed Polyvinyl acetate	Starch grafting
Polyurethane	Starch modification
Hydrolyzed EVA polymer	Starch modification
Polyesters (Polyglycolic acid, poly-l-lactic acid) citric acid copolymers, poly-hydroxybutyrate	

Fig. 3: Mechanism for biodegradation. Presence of Hydrolyzable groups or linkages such as amide, ester, urea, hydroxy, benzyl etc. of both hydrophilic and hydrophobic segments and of amorphous zones in polymers helps in biodegradation.

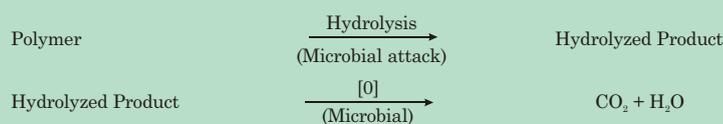


Table 3 : Early Manufacturers of Biodegradable Plastics

Manufacturer	Trade name of the product
Warner-Lambert Company, USA Amko Plastics, USA Air products & Chemicals, USA Agrico Chemical Company, USA Novamont, Italy	Novon (Molding Grade) Polybioethylene Mater - B1 (Molding Grade) Cornplast (masterbatch)
Cabot Europe Ltd., France Exxon Chemical, Belgium Rhone-Poulenc Chemie, Belgium Hoechst, Germany Nova Corporation, Canada	

Table 4 : Potential Applications of Biodegradable Polymers

Area of use	Product form	Application
Agriculture	Fiber	Netting
	Film	Mulching Controlled release of agrochemicals and micronutrients
Horticulture	Film	Nursery bags
	Molded products	Plant covers and plant holders
Packaging	Film	Packaging of perishable foods, dairy products, fruits, vegetables, hosiery etc.
	Blister packaging sheets and bubble films	Fragile goods packaging
Domestic	Films	Shopping bags, composting bags, diapers, feminine hygiene products, garbage bags
	Molded products food service items	Food containers, vegetable crates, egg boxes, toys, pens, cutlery and cups, razors, containers for beverages etc.
Hospital	Molded products	Disposable needles and syringes sutures, surgical gowns etc.

Though there is a necessity of development of Biodegradable Polymers mainly for short life uses, there is a conflicting situation between recycling and biodegradation.

It is apprehended by many that bio-degradable polymers may find their way into the waste stream in the initial stages (as degradation does not take immediately) and get mixed with recyclable plastics, making it unsuitable / less suitable for applications for longer duration.

This remains as one of the concerns of development of Biodegradable plastics.

DID YOU KNOW?
About 0.1 million tonnes of Municipal Solid Waste is generated in India everyday



ICPE Initiative

Retailers give away thousands of carry bags to shoppers in Mumbai and elsewhere. Now in an effort to inculcate civic consciousness amongst our citizens, bag manufacturers would be displaying 'This bag can be recycled. Dispose it responsibly' logo on plastic bags: so that after use of the bag they will dispose it in a responsible manner.

ICPE has always endeavored to keep our environment clean and provides the necessary infrastructure to tackle the challenges of waste management and encourage the responsible use and disposal of all material, including plastics and plastic bags. This is yet another attempt on its part to work on standards and specifications on recycling of plastic waste and collaborate with the industry in creating greater widespread awareness about litter and waste segregation.



Biodegradability: Myths and Realities

What is biodegradability of polymers and what are its merits and demerits?

Biodegradability of polymers is the ability of micro-organisms to metabolise organic polymeric materials to innocuous products. Biodegradability implies that no toxic residues are left in the landfill or compost pit at the end of the biodegradation process. Ideally, an organic polymer when subjected to biodegradation in presence of air (aerobic bacterial process) must convert all the carbon of the polymer to carbon dioxide; whereas, in the absence of air (anaerobic bacterial process) must convert all the carbon of the polymer to methane. The former process occurs in landfills, whereas the latter process is prevalent in composting pits.

True biodegradability of a material in a composting environment renders waste disposal easy and converts organic wastes into useful products like biogas and organic manure. It is safer and cost effective as compared to incineration or land filling.

What are the challenges that face biodegradable polymers?

Most organic polymers are not biodegradable either aerobically or anaerobically. This is because organic polymers were originally designed to replace scarce natural

materials like wood, silk and cotton or materials that consume substantial amount of energy and other scarce natural resources for their manufacture, such as metal, paper and glass. For several applications of polymers such as structural materials, polymers need to have a long life. Hence, biodegradability is not desired in all applications of polymers. On the other hand, biodegradability is a desirable attribute for a polymer whose service life is short.

However as of today truly biodegradable polymers that have all the property attributes of hydrocarbon-based polymers are very rare. The challenge is to create biodegradable polymers with a diversity of properties available from non-biodegradable polymers.

Is the basis of biodegradability or eco-friendliness of materials used properly understood of people? Please comment.

Biodegradability and eco-friendliness of materials are misunderstood by many, including the common man. To bring real meaning into the discussion, we must shift the debate from material attributes to material waste disposal issues. Also, to talk about biodegradability without defining the final resting place of the material is pointless. This implies

that we must have clear uniform guidelines and understanding as to where each of the materials that we consume finally ends up after its use. Biodegradability must also be application specific and is not needed for all polymer applications. Biodegradability must have one clear scientific definition. We must have test methods and standards that can qualify such materials. Biodegradability also has a dimension of time. One must define the time period within which the polymer needs to be completely metabolized. Many people do not realize that even polyethylene, if left in the environment for a sufficiently long time, will degrade into innocuous products under the combined action of light, heat and microorganisms.

Is the industry taking any initiatives to address the issues relating to biodegradable polymers and their applications?

The plastic industry has taken several initiatives to educate the public and lawmakers on the benefits of plastics. It has also advocated responsible urban waste handling systems to be implemented by the Municipal Corporations. The industry at the same time must also advocate the principles of 3 Rs namely- Reduce, Reuse and Recycle especially for plastics, which have a short service life.



Dr S. Sivaram
Director, National Chemical Laboratory, Pune

Misinformation that can build up mis-perceptions.

'Stored blood in PVC bags risk to patients'

Recently newspapers carried a report by a Thiruvananthapuram based company, on how patients receiving frequent transfusions of blood stored in polyvinyl chloride (PVC) bags, normally supplied by blood banks, are exposed to the risk of developing brain disorders.

The report states that during manufacture, PVC uses a chemical called DEHP as a plasticizer. Significant amount of this chemical (as much as 0.15 gram per litre of blood) leaches out into the blood.

The Truth is...

The International Agency for Research on Cancer (IARC) which is a part of WHO says, that DEHP {Di(2-Ethylhexyl) Pthalate} not classifiable to carcinogenicity to humans. It belongs to a structurally diverse group of compounds that induce peroxisome proliferation in the liver of mice and rats, but not in other rodent and non-rodent species that have been tested and not in the human liver tissue. This IARC decision was taken by a group of 28 experts from 28 countries that met in Lyon, France in February 2000. (<http://www.ecpi.org/pressrelease/details/index.asp?id=4>)

Also the American Council on Science and Health convened an independent panel (in 1999) to evaluate the scientific evidence regarding potential health risks associated with DEHP found that it is a primary plasticizer used in many medical devices, which is not harmful and imparts a wide variety of physical characteristics that are critical to the function of medical devices. The mechanism by which DEHP increases the incidence of tumours in rats and mice is not relevant to humans.

For over 40 years, plastic medical products from disposable syringes to intravenous fluid and blood bags to heart valves have helped doctors and nurses save innumerable lives, and make better and longer lives a reality for the rich and the poor in developed and developing nations. These plastics have to adhere to very stringent standards and must be non-toxic, non-carcinogenic, biocompatible, and are in no way injurious in the biological environment.



Cow's Milk.
Rich in toxic dye.



ICPE IMPACT

ASCI upholds the DPCC ads released in Delhi papers

A few months ago the Delhi Pollution Control Committee (DPCC) issued advertisements in some newspapers on how plastic bags are causing havoc not only to our environment but also affecting stray animals. The ad showed a cow rummaging for food at garbage dump stating " Cow's milk. Rich in

Toxic dye" suggesting that plastics bags contain toxic dyes and when ingested by the cow can contaminate the milk produced by the cow, "leading to serious health problems". While we at ICPE have no quarrel with anyone urging people to use cloth, jute or even steel mesh bags, ICPE objected to the advertisement claiming that, "The plastic bag that you used yesterday could find its way into your cup of tea

today." We all know that cows that wander city streets are generally those that have been abandoned by their owners because they are no longer of use as milch cattle. Besides garbage also contains paper, pins, nails, glass, tins, cardboard, batteries, rags, leather and even faeces that such cows inadvertently consume? These materials are as toxic, if not more, whilst the ad targeted only plastic. Recent studies also indicate that plastics account for less than 6% of the waste in our cities - so the cow could very well be poisoned by the remaining 94% of waste! ICPE, AIPMA and IPI took up the matter with the Advertising Standards Council of India (ASCI) highlighting the fact that the advertisement will mislead the public and cause unnecessary fear in the minds of the public. ASCI has upheld the complaint stating '**the complaint was UPHELD** as the advertisement contravened Chapter 1.4 of the code.'

INDIA

Ragpickers get training in garbage management

Mumbai's 14 million people generate 6,000 metric tonnes of garbage in the city daily. That's what makes the work of Avinash Kubal relevant for them. The deputy director of the Maharashtra Nature Park at Dharavi took a step towards reducing the city's sprawling garbage problem when he decided to marshal the resources of its one lakh-odd ragpickers last year.

He designed a three-month training programme for them in garbage segregation, composting and vermiculture, and gardening. "I thought of ragpickers for garbage management because they work in this field and have no hangups about it," said Mr Kubal. "They already segregate and recycle non-biodegradable garbage. We train them to segregate and treat organic garbage, which forms 40 per cent of the total and creates the problems of pests and diseases. We teach them how to convert this to manure, which can be sold, too."

Mr Kubal and several volunteer horticulturists have already trained about 600 ragpickers. The classes, in batches of 50, are held in the afternoon at the Nature Park. The training is purely practical.

NGOs like Stree Mukti Sanghatana and Aakar Mumbai help convince ragpickers to attend the classes. Although many aren't interested to start off with, their motivation levels rise when they realise they can earn money by learning the skills taught to them. The classes aim to place the trained ragpickers at various housing societies in Mumbai. "If three or four trained ragpickers are adopted by each big housing society, they could keep the neighbourhood clean by collecting the society's garbage, segregating it and maintaining the composting pits-which we'll set up initially, with the society's help," said Mr Kubal. "This will solve the problem of stink, garbage transportation to dumping grounds and scavenging animals like rats, cats and dogs. The manure produced can be used for gardening if the society has one, or sold."

The payment module proposed by Mr Kubal to housing societies doesn't include a regular salary. Instead, the ragpickers collect Rs 30 to Rs 40 from each flat every month for taking care of their garbage-perhaps more, if they sweep the common areas. Besides this, they earn by selling Non-biodegradable garbage and manure.

Have there been any takers yet? "Some societies in Chembur, Ghatkopar and Andheri and the Reserve Bank colonies of Malad and Dahisar have accepted our proposal, and have given good feedback," he replied. "The numbers are few because it requires breaking through social attitudes." Some societies insist that garbage management is the BMC's responsibility not theirs, some wrongly believe that composting pits stink, while some feel ragpickers cannot be trusted.

Mr Kubal has solved the last problem by making himself and his colleagues accountable for every ragpicker passing out of his programme.

He has the details of every person in his database. "Our request to all colonies is that they take the help of local NGOs to identify ragpickers in their area and send them to us for training," said Mr Kubal. "After three months, the same people will keep their neighbourhood clean."

The Times of India, Mumbai, August 20, 2003



DID YOU KNOW?
Per capita waste generation in major Indian cities ranges from 200gm to 600gm

INTERNATIONAL

Plastic Chips: New materials boost organic electronics

Over the past decade, research groups in academia and industry have been racing to fabricate electronic devices—integrated circuits, displays for handheld computers, and solar cells—not from silicon but from semiconducting polymers. Components made from such organic materials could be flexible, as well as cheaper and easier to manufacture than their silicon counterparts. Now researchers at Northwestern University in Evanston, Ill., and Lucent Technologies in Murray Hill, N.J., have devised a new class of organic semiconductor materials that could hasten the arrival of what could be the electronics revolution's next big wave. Until recently, the fabrication of plastic electronics has been limited by the number of molecular building blocks suitable for making semiconducting polymers. Transistors—which are the switches in an integrated circuit—require two types of semiconductor materials: n-type and p-type. In n-type materials, charge flows through the material via electrons. But p-type materials transport charge through "holes," places where electrons are missing.

"Yet, most of the organic materials examined so far have all been p-type," says lead investigator Tobin Marks at



Northwestern. Existing n-type organics are rare and unstable. "So there's a real need for n-type materials," he says. His team's new class of molecules assembles into semiconductors of both p- and n-type. A rod-shaped organic molecule made of six thiophene units forms the basis for each type of material. Each thiophene, in turn, is a ring of 5 units of carbons and 1 unit of sulphur. When the researchers replaced the rod's two end thiophenes with a perfluoroarene group (a ring of six carbons decorated with fluorines), the organic molecule behaved like an n-type semiconductor. When the researchers instead replaced the next two thiophenes from the ends, the molecule behaved as a p-type semiconductor. "It turns out, the way we move the perfluoroarenes around also allows us to control the packing between the molecules," says Marks.

The closer the molecules are to each other, the faster a charge can hop from one molecule to another in either type of semiconductor. So far, the team has fabricated prototype transistors from the materials, which performed just as well as existing organic semiconductors do, as measured by the mobility of the electrons and holes. But Marks says his lab expects to increase the n-type material's electron mobility by at least a factor of 5, an advance that would boost the switching speed of the material. The array of organic materials for making n-type semiconductors has been particularly sparse, says Ananth Dodabalapur of the University of Texas at Austin. "This will be very useful for people like myself who make organic circuits."

One of the biggest appeals of plastic electronics is that manufacturers could spray liquid polymer circuits onto a surface using ink-jet printers, instead of resorting to the multibillion-dollar fabrication equipment used to etch circuitry on silicon wafers.

[Http://www.sciencenews.org/20030830/fob5.asp](http://www.sciencenews.org/20030830/fob5.asp)

Press 'n' Peel Lasers: Coaxing light beams out of cheap plastic

Like poker chips, lasers may someday be molded out of plastic by the millions. A new laser-making method takes a major step in that direction, its Austrian developers say. Lasers are devices that emit a coherent beam of light of a single wavelength. Their prices have been coming down over the years, but dirt cheap plastic ones could serve as the heart of mass-produced biomedical and environmental sensors and optical-telecommunications networks, the researchers say. What's more, unlike the lasers currently available, plastic ones could be flexible.

DID YOU KNOW?

Out of the total municipal waste collected, on an average 95% is dumped on land and 5% is composted

Manufacturers today rely on costly fabrication techniques for making the microchip lasers used widely in CD and DVD players and other gadgets. Those techniques require exacting procedures carried out in tightly controlled conditions and meticulously clean environments.

In the July 17 *Advanced Materials* issue, Martin Gaal and Emil J.W. List of the Graz University of Technology and their colleagues describe a simpler method of making lasers by imprinting patterns into plastic under ordinary conditions. The Graz scientists had teamed up with researchers from AT&S, a circuit board maker in Leoben, Austria. The key to the new technique is a hard mold with a shallow grating on its surface. The nanometer-scale depths and spacing of the ultra fine, parallel ridges provide a fine structure that stimulates laser action.

To make each laser, the researchers press their mold into a droplet of solution. It contains a semiconducting polymer, known by the acronym MEH-PPV, that has been dissolved in a fast-evaporating solvent. When the coating dries, the polymer retains a negative replica of the mold's ridges. That structure, which the researchers peel from the mold, acts as a laser. "You can imagine the grating as if it was a fingerprint," says List, who led the team. "The real step forward is the ease of fabrication," he notes. "You have nanostructures that you just press into the material. You can do it once, twice, many times. That makes the entire process very cheap." The tough part is producing a mold with precise nanoscale ridges only 30 nanometers high and roughly 400 nm apart. To do this, the scientists rely on the same photolithographic techniques used to make microchips.

A drawback of the new approach is that the resulting lasers produce light only when stimulated by another laser. Most lasers now in use produce light directly from an electric current. List says that researchers in his lab and many others are already racing to invent electrically driven lasers made out of polymers such as MEH-PPV. The fabrication method of the Austrian team is not entirely new, notes John A. Rogers of the University of Illinois at Urbana-Champaign. He and his colleagues have used the same approach to create relatively coarse-structured, non-laser light sources in various shapes, such as rings. Yet List and his coworkers have attained much finer structural features and created patterns that can support laser action, Rogers says. "Those are both... impressive demonstrations," he adds.

www.sciencenews.org/20030726/job5ref.asp



DID YOU KNOW?

**The Calorific value
of Indian
solid waste is
between 600 and
800 Kcal/kg**

ICPE NEWS

In India around 4 million kilo tonnes of plastic materials are consumed each year with packaging forming the largest market for plastics, accounting for over 30% of the consumption of raw plastic materials. Plastic packaging provides excellent protection for the product, is cheap to manufacture, seems to last forever and provides great reliability in use.

In order to provide exhaustive information, a compendium on **Plastics in Food and Healthcare Packaging** has been brought out by ICPE providing detailed information on the use of Plastics in Safe Packaging of food and healthcare products. The four volume compendium contains published articles, list of Indian and International Standards and Research Papers.



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