Chapter - VIII

APPENDIX- I LIST OF PUBLICATIONS

1. Colony growth on LDPE Specimen, **Shah G.D.** Modern Plastics & Polymers, Feb-Mar 2007.pp70-72.
2. Biodegradable Polymers, **Shah G.D.** Popular Plastics & Packaging, March - 07. pp 95-99.
3. Theory of Polymer Degradation, **Shah G.D.** Modern Plastics India Magazine, March 2007. pp 49-50.
4. Biodegradability of LDPE: Tests as per ASTM G-21, **Shah G.D.,** Modern Plastics & Polymers, April-May 2007.pp70-72.
5. Use Plastics- Save Environment, **Shah G.D.** Popular Plastics & Packaging, May - 07. pp 104-108.
6. Testing Protocols for Biodegradation, **Shah G.D.** Modern Plastics India Magazine, May 2007. pp 48-50.
7. Recycling Of Plastics-A Solution to Waste Management **Shah G.D.** Popular Plastics & Packaging, June - 07. pp 102-106.
8. Waste Management of Plastic Material **Shah G.D.** Popular Plastics & Packaging, August- 07. pp 91-94.
9. Biodegradable Low Density Polyethylene **Shah G.D** **Paper accepted for** Progress in Rubber, Plastics & Recycling Technology, Smithers **Rapra Technology UK** and publication is anticipated in the middle of 2008.
10. Biodegradable Polymers In Medical Application **Shah G.D.** Popular Plastics & Packaging, September- 07. pp 53-56.

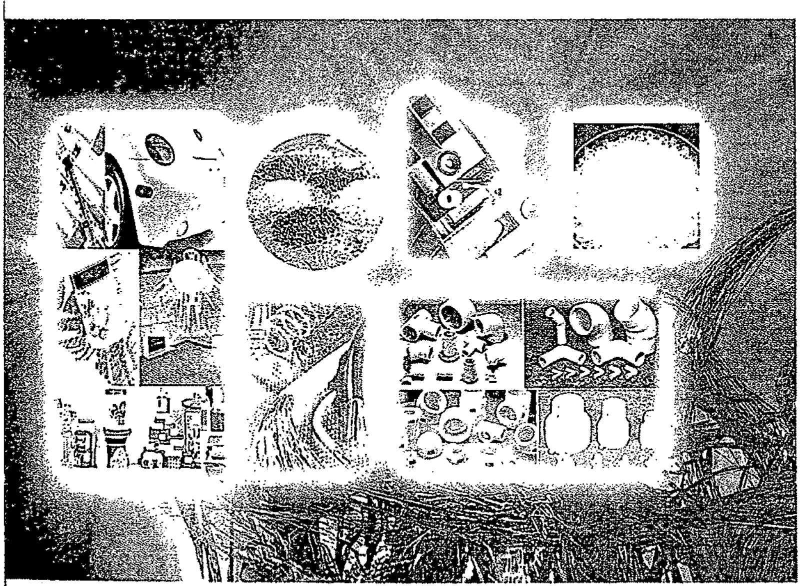
Colony growth on LDPE specimen

The biodegradability test

In early years, biodegradability was assessed by observing microbial growth, weight loss and change in strength. All these indirect measurements were difficult to reproduce in laboratories. This created confusion in terms of susceptibility towards biodegradation of a given polymer. Today, there are a number of international standards and test methods, which have been developed specifically for biodegradability. The colony growth profile in broth medium as per ISO 846 Method A assesses the ability of plastics to act as a nutritive medium for fungi. LDPE compounded with various plasticisers was subjected to growth profile test and the amount of growth was measured. Read on...

G D Shah

Today, the market for polyolefins like LDPE, HDPE and PP microfilms used as packaging carrybags is very wide. Polyolefin in its unmodified form is resistant to destruction by biological agents. From the environmental viewpoint, it would be highly beneficial if these films were biodegradable and decomposed almost completely under the attack of microorganism over a period of few months. Since all polymers degrade in one way or the other, they are considered as degradable. But in practice, if a polymer does not degrade within human lifetime, it is usually considered non-degradable.



Theory of degradation

Polymers have been modified to develop environmentally acceptable polymers. The modification includes blends with other natural and synthetic polymers, grafting of another polymeric composition and chemical modification to introduce desirable functional group by oxidation or some other simple chemical reaction such as esterification or etherification. Synthetic polymers are inherently resistant to biological attack. But susceptibility to biodegradation varies and is affected by additives, plasticisers, the type of chemical bond, water uptake, crystallinity & molecular weight, pH, copolymer composition and enzymatic degradation.

Action of plasticisers

Plasticisers are occasionally used as processing aids in highly cross-linked polymers. Plasticisers appear to function in polar, mainly by masking polar sites in the chain and thereby reducing hydrogen bonding. In all polymers, plasticisers tend to force the chain apart, giving them greater freedom of movement and also reducing Van Der Waals forces between the chains. There are no plasticisers that are completely free from fungal or bacterial attacks. Susceptibility of microbial attack increases as the plasticiser level increases.

Experiment

- A fully biodegradable polymer containing a minimal amount of plasticiser was developed
- The biodegradability of the polymer with respect to amount, duration and type of plasticiser was checked

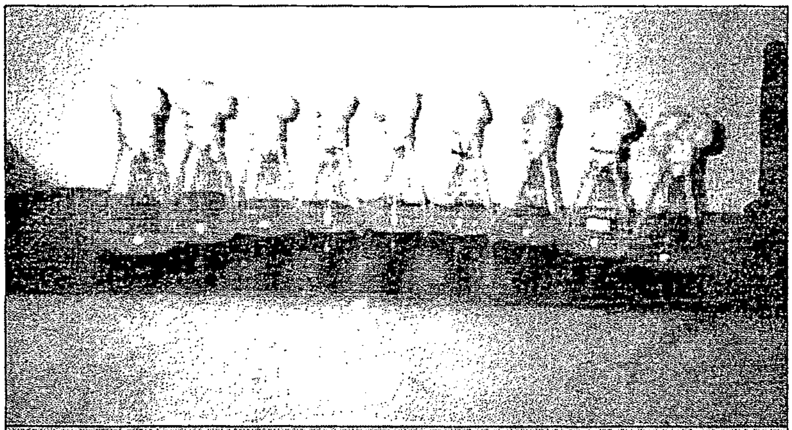


Figure 1: Experimental set up for colony growth profile in broth medium; different turbidity is seen in each flask

- The microbial susceptibility of various plasticisers was checked
- The approximation of plasticiser concentration, which exhibits highest susceptibility towards microbial attack was observed

Process description

- LDPE having the highest market for carry bags was selected as the base polymer. Amongst the most susceptible plasticisers, the following eight plasticisers were selected on the basis of availability and cost that was comparable with LDPE. These included butyl stearate, cottonseed oil, dioctyl phthalate, epoxidised soyabeen oil, linseed oil, soyabeen oil, groundnut oil and general purpose polyester
- Ten samples from each plasticiser were prepared with varying amounts of plasticiser. These 80 samples were tested for biodegradability with six different organisms, viz, pseudomonas aeruginosa, staphylococcus aureus, e-coli, aspergillus niger, penicillium, and mixed culture of the above microorganism
- The specimens were subjected to screening of biodegradation of specimen in open air for one month and were under agitation for eight weeks
- The medium from the screening test was collected in a flask. The flask was placed on the shaker for continuous stirring for three days so that all the nutrients get exhausted. Further, a mixed culture of adopted microorganism was prepared for testing of colony growth profile
- Eight samples with the highest concentration were selected as reference specimen. Mixed culture without nutrition was mixed with tap water in nine different conical flasks
- Reference optical density in spectrometer was set by tap water, and was kept as control
- Specimen with the highest plasticiser concentration was placed in the rest of the eight flasks containing the culture and water mixture. The ninth flask was kept as reference or control
- The optical density of the medium in each flask was measured and recorded as the initial OD in nanometer
- The conical flasks were placed on a shaker for continuous stirring at 31.3°C and 125 rpm
- The optical density was measured after one, three & eight weeks, and recorded
- The increase in turbidity was inferred as the colony growth due to specimen. Ie, the microorganisms get nutrition from the specimen and hence are growing.

Results

The specimens containing linseed oil, soyabeen oil and groundnut oil showed the highest, as well as a gradual rise in turbidity. Hence, it recorded the highest susceptibility towards biodegradation. The specimen containing butyl stearate showed moderate susceptibility towards biodegradation. Specimens with all other plasticisers too showed gradual but small rise in turbidity. Thus, the adopted microorganism gets nutrition from the specimen material. Further, experimentation can be carried out using other plastic material using this adopted culture.

Inference

The basic principle of this experiment is that when a plasticiser is included in the plastic composition, it improves the extensibility of the plastics melt by way of sliding the polymer chains over each other. This sliding of chains in turn reduces the overall tensile strength of plastics by way of reducing the binding forces between the two adjacent chains. When these binding forces between the chains are reduced, it will be easier for the microorganism to attack on the weakened, individual chains and get nutrition for growth. Thus, the degradation process can be continued.

Table 1: Results for colony growth profile on specimen in broth medium

Specimen	OD at 460 Nm			
	Initial	1 week	3 week	8 week
Control	0.346	0.337	0.440	0.228
Butyl stearate	0.352	0.152	0.509	0.567
Cottonseed oil	0.354	0.400	0.553	0.563
Dioctyl phthalate	0.344	0.441	0.669	0.689
Epoxidised soy been oil	0.395	0.256	0.342	0.353
Linseed oil	0.047	0.084	0.163	0.257
Soyabeen oil	0.417	0.423	0.486	0.555
Groundnut oil	0.433	0.413	0.649	0.749
GP polyester	0.414	0.209	0.230	0.381

The initial nutrition was obtained from the plasticiser, which exuded from the plastic specimen. The plasticiser, when exuded out of the polymeric chains, left space between the chains. This in turn increased the distance between the chains, thus further weakening the binding forces between the chains.

Future scope of research

Other test methods for assessing biodegradability should be employed like:

- Screening of biodegradation of specimen in open air
- Screening of biodegradation of specimen under agitation
- Growth rating ASTM G-21
- Soil burial test

Individual microorganism can be separated and their biodegradability can be checked individually. New micro flora can be developed by growing adopted microorganism in the soil nutrition by the plastics specimen. This microorganism can further be developed individually and characterised by their ability and the rate of biodegradability of the plastic films. The film thickness, plasticiser concentration, commercial production and cost effectiveness also can be optimised.

Biodegradability of other plastic materials like PP, HDPE, GPPS, LLDPE, HMHDPE, etc, can be tested using the same plasticisers, ie, butyl stearate, soyabeen oil, linseed oil, groundnut oil, etc.

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MPP

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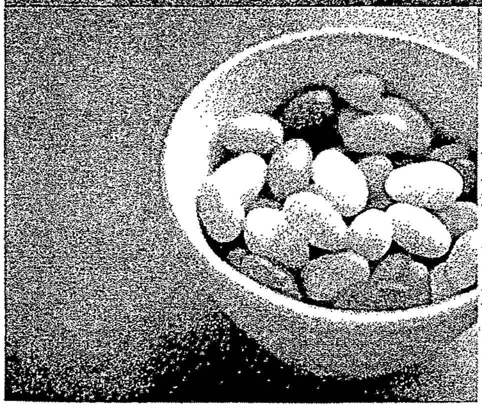

Biodegradable Polymers

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Abstract

Biodegradable polymers can be classified into natural polymers, synthetic polymers and modified natural polymers. Various biodegradable polymers are described with respect to their composition, structure, properties and applicability.

TODAY polymer industry is facing environmental problems. Most of the polymer does not degrade under standard environmental conditions. Yet it would be interesting to know about various polymers that degrade in biological environment. Also by increasing their use the environmental problems can be resolved to a certain extent.

Classification of biodegradable polymers

Biodegradable polymers can be divided into three broad classifications:

1. Natural polymers
2. Synthetic polymers
3. Modified Natural polymers

These classes may be further subdivided as:

1. Natural polymers or biopolymers
2. Synthetic polymers
   (a) Carbon chain backbone
   (b) Heteroatom chain backbones
3. Modified Natural polymers
   (a) Blends and grafts
   (b) Chemically modified
   (c) Oxidation
   (d) Esterification

Natural polymers or biopolymers

They are produced naturally by all living organisms. They are environmentally acceptable degradable polymers. Most common natural polymers are:

1.	Polysaccharides	starch and cellulose
2.	Polyesters	polyhydroxyalkanoates
3.	Proteins	silk and poly (2-Glutamic acid)
4.	Hydrocarbons	natural rubbers

Polysaccharides

They are largely limited to starch and cellulose derivatives for practical applications either in plastics or as a water-soluble polymers. Both these polymers are composed of D-Glycopyranoside repeating units to very high molecular weight, thousands of units. They differ in that starch is poly (1,4-2-D-Glucopyranoside) and cellulose is poly (1,4-B-D-Glucopyranoside). This difference in structure control biodegradation rates and properties of the polymers. Complex carbohydrates like microbially produced xanthan, curdlan, pullulan, hylauranic acid alginates, carageenan and guar are accepted biodegradable polymers. Xanthan is the prominent microbial polysaccharide and finds use in the food industry. It is also used as a thickener in many industrial applications.

Proteins

They must be used as found in nature because they are not soluble or fusible without decomposition. They are widely used as fibers e.g. wool, silk, gelatin (collagen) which is used as an encapsulate in the pharmaceutical and food industry. The structure of proteins is an extended chain of amino acid joined through amide linkages that are readily degraded by enzymes, particularly protease. Recent activity in poly (r-glatanic acid) with control of stereo chemistry. The inclusion of manganese ions may be important for future development in biodegradable water-soluble polymers with carboxyl functionality.

Polyesters

They are produced by many bacteria as intracellular reserve material for use as a food source during periods of environmental stress. They are biodegradable, can be processed as plastic materials, are produced from renewable resources and can be produced by many bacteria in a range of composition. The thermoplastic polymers vary from soft elastomer to rigid brittle plastics in accordance with the structure of the pendent side-chain of the polyester. All the polyesters are 100% optically pure and are 100% isotactic. Longer side chain polyesters are produced by variety of bacteria, usually as copolymers and with low crystallinity, low melting points and low Tg. These polyesters are elastomeric and have excellent toughness and strength. They are inherently biodegradable. But as the chain length increases the rate of biodegradation is greatly reduced.

Synthetic Polymers

Synthetic polymers do not have natural origin, the plethora of enzymes available in nature for degrading natural polymers are not useful for synthetic polymers. Researches are carried out for synthetic polymeric structure that can be biodegraded. Some guidelines based on polymer structure, polymer physical properties and environmental conditions at the exposure sites have emerged for polymer structure. Following generalization can be made:

1. A higher hydrophilic/hydrophobic ration is better for degradation.
2. Carbon chain polymers are unlikely to biodegrade.
3. Chain branching is deleterious to biodegradation.
4. Condensation polymerization is more unlikely to biodegrade.
5. Lower molecular weight polymers are more susceptible to biodegradation.
6. Crystallinity reduces biodegradability.

Favorable polymer physical properties include water solubility and sample purity. Environmental conditions to be considered in evaluation of biodegradability are temperature, pH, moisture, oxygen, nutrients, suitable microbial population, concentration and test duration.

Polymers with carbon backbones

These polymers may be represented by and is considered derivatives of PE. Where 'n' is the degree of polymerization and 'R' is the functional group. The functional groups and the molecular weight of the polymer control their properties that vary in hydrophobicity, solubility characteristics, Tg and crystalinity.

Polyethylenes

Fungal and bacterial growth tests indicate that polyethylene and other high molecular weight carbon chain polymers do not support growth. Anomalous results were observed when plasticizers or low molecular weight impurities were added. It was also found that branching of hydrocarbon chains limits biodegradation. There is an increase in biodegradation with lower molecular weight because of the transportation of polymer across cell wall is more likely at lower molecular weight or it may be the mechanism of biodegradation or because of random or chain end cleavage prior to entering the cell. The slow biodegradation process in PE can be accelerated with surfactants or an oxidation process.

Vinyl Polymers

Their biodegradation requires an oxidation process and most of the biodegradable vinyl polymers contain an easily oxidisable functional group. To improve biodegradability of vinyl polymers, catalysts are added to promote their oxidation or photodegradation or both. Incorporation of photosensitive groups like ketones into the polymers is also attempted.

Polyvinyl Alcohol

It is the most readily biodegradable of vinyl polymers. It is readily degraded in wastewater activated sludge. The microbial degradation of PVAL has been studied. Its enzymatic degradation by secondary alcohol peroxide isolated from soil bacteria of the pseudomonas strain is also studied. The initial step involves the enzymatic oxidation of the secondary alcohol groups in PVA_L to ketone groups. Hydrolysis of ketone groups results in chain cleavage. Other bacterial strain, such as flavobacterium and azetobacter were effective in degrading PVA_L.

PEK

Controlled chemical oxidation of PVA_L into PEK. It has similar structure to the intermediate formed as PVA_L is biodegraded. PEK is found more susceptible to hydrolysis and biodegradation than PVA_L. It is the polymeric form of acetoacetone, hence it forms metal chelate. Its water solubility, reactivity and biodegradability make it potentially useful material in biomedical, agricultural and water treatment areas. By using dyes as model it was found that PEK and PCL blends are excellent controlled release systems.

Polyvinyl Acetate

PVA_L is obtained from hydrolysis of polyvinyl acetate. Controlled hydrolysis of PVAc followed by oxidation provides degradation material having a wide range of properties and degradability. PVAc undergoes slow biodegradation in soil burial tests. The weight loss increases with the acetate content.

Polyacrylates

Polyalkyl acrylates and polycyanoacrylates generally resist biodegradation. Weight loss in soil burial test is reported for copolymers of ethylene and propylene with acrylic acid, acrylonitride and acrylamide poly alkyl 2-cyanoacrylates. Polymethyl 2- cyanoacrylate is the most degradable among the esters. The degradability decreases as the alkyl size increases. Poly iso beetyl 2- cyanoacrylate nano particles is degraded in two enzyme free media a pH 7 and pH12 in the presence of rat liver microsomes.Poly 2-hydroxy ethyl methacrylate is generally cross-linked with a small amount of ethylene dimethacrylate. It swells in water to form a hydrogel and is widely used in biomedical area due to its good biocompatibility.

Heteroatom chain backbone polymers

Their linkages are quite frequently found in nature and they are more likely to biodegrade than hydrocarbon based polymers. They include polyesters, polyamides, polyethers, polyacetates and other condensation polymers.

Polyesters

Aliphatic polyesters are the most easily biodegraded synthetic polymers known.

Table: Biodegradable polyesters in commercial development

PHA	polyhydroxyalkanoates
PHB	polyhydroxybutyrate
PHH	polyhydroxyhexanoate
PHV	polyhydroxyvalerate
PLA	polylactic acid
PCL	polycaprolactone
PBS	polybutylene succinate
PBSA	polybutylene succinate adipate
AAC	Aliphatic-Aromatic copolyesters
PET	polyethylene terephthalate
PBAT	polybutylene adipate/terephthalate
PTMAT	polymethylene adipate/terephthalate
PGA	polyglycolic acid
PLLA	poly (L- lactic acid)

The simplest poly (α-hydroxyacid), polyglycolic acid (PGA) has been successfully used as biodegradable suture. The partially crystalline polyester is generally obtained from the polymerisation of diglycolide with a tin catalyst. Also poly (L-lactic acid) PLLA is obtained from dilactide and is used as suture. Aromatic polyesters such as PET exhibit excellent material properties, they prove to be almost totally resistant to microbial attack. Aliphatic polyesters on the other hand are readily biodegradable, but lack good mechanical properties that are critical for most applications. All polyesters degrade eventually, with hydrolysis (degradation induced by water) being the dominant mechanism. Synthetic aliphatic polyesters are synthesised from diols and dicarboxylic acids via condensation polymerisation, and are known to be completely biodegradable in soil and water. These aliphatic polyesters are, however, much more expensive and lack mechanical strength compared with conventional plastics such as polyethylene.

Polyurethanes

Polyester based polyurethanes are more susceptible to degradation than those derived from polyether diols. As the flexibility of polyurethane increases, their susceptibility towards biodegradability increases. Polyamide urethane prepared from amino alcohols are easily degraded by substilin.

Polyamides

Nylon 6, Nylon 6,6 generally resist microbial and enzymatic attacks but oligomers of e-amino hexanoic acid are degraded by enzymes and microorganism. The loss of tensile strength of nylon in vivo is by 25% after 89 days and 83% after 726 days. Etching of a nylon fiber after 210 days in vivo is also seen. In vivo degradation of nylon is caused by hydrolysis and proteolytic enzyme catalysis. Incorporation of methyl, hydroxy and benzyl groups into polyamide chains improves the biodegradability. Biodegradability of polyamide esters decreases by shortening polyamide blocks and increasing polyamide content.

Polyureas

Polyureas prepared from lysine esters with 1,6 hexane diisocyanate are readily degradable and is used in polymer drug application. The polyester urea from phenylamine containing hydrophobic benzyl group is readily hydrolyzed while unsubstituted polyester urea from glyline is not affected.

Polyanhydrides

Fibre forming polyanhydrides are very susceptible to hydrolysis. Poly[bis-(p-carboxyphenoxy)methane] - PCPM was examined as matrix material for controlled release of drugs and was found to erode slightly faster in vivo than in vitro buffer. The erosion of PCPM is mostly heterogenous surface erosion which gives a near zero order released rate.

Poly (Amide-Enamine) s

Homogeneous erosion of hydrophilic biodegradable polymer matrix system undergo progressive loosening or swelling. Hence by surface erosion, a near zero order release can be obtained if diffusion release is small. Poly [amide-enamine]s are are found susceptible to hydrolysis and biodegradation.

Polyphosphagene

The polymer contains phosphorous nitrogen chains. They are readily hydrolyzed to give phosphoric acid and ammonia derivatives.

Modified natural polymers

Natural polymers are modified so that the environmentally acceptable polymer can be developed. Hence the modification should not interfere the biodegradation process. The modification includes blends with other natural and synthetic polymers, grafting of other polymeric composition and chemical modification to introduce some desirable functional group by oxidation or some other simple chemical reaction such as esterification or etherification.

Starch

Starch is made thermoplastic at elevated temperature in the presence of water as a plasticizer, allowing melt processing alone or in blends with other thermoplastic. Water lowers the melt transition temperature of starch so that processing can be done well below the degradation temperature.

Starch-PE Blends

The most important commercial application is the blending of PE with starch in presence or absence of other additives. The starch -PE are compatibilized with:

1. Ethylene acrylic acid copolymer
2. Ethylene vinyl alcohol polymers
3. Hydroxyacids
4. Urethanes
5. Polyamides
6. Polyvinyls
7. Cellulose acetate
8. Alkyds
9. Polycaprolactone

The product based on this chemistry are characterized by incomplete biodegradation, water sensitivity.

Other Blends

The blending composition is limited only by number of polymers and the compatibility of the components.

1. PHA with cellulose acetate
2. PHA with PCL
3. PLA with PEG
4. Chitosan with Cellulose
5. PLA with inorganic fillers
6. PHA and aliphatic polyesters with inorganics

Naturally produced polymers

PHA

Polyhydroxyalkanoates (PHAs) are aliphatic polyesters naturally produced via a microbial process on sugar-based medium, where they act as carbon and energy storage material in bacteria.They were the first biodegradable polyesters to be utilised in plastics.

PHB/PHV

The two main members of the PHA family are polyhydroxybutyrate (PHB) and polyhydroxyvalerate (PHV). Aliphatic polyesters such as PHAs, and more specifically homopolymers and copolymers of hydroxybutyric acid and hydroxyvaleric acid, have been proven to be readily biodegradable. Such polymers are actually synthesised by microbes, with the polymer accumulating in the microbes' cells during growth. The most common commercial PHA consists of a copolymer PHB/PHV together with a plasticiser/softener and inorganic additives such as titanium dioxide and calcium carbonate. A major factor in the competition between PHAs and petroleum based plastics is in production costs. Opportunities exist however for obtaining cheaper raw materials that could reduce PHA production costs. Such raw materials include corn-steeped liquor, molasses and even activated sludge. These materials are relatively inexpensive nutrient sources for the bacteria that synthesise PHAs. The PHB homopolymer is a stiff and rather brittle polymer of high crystallinity, whose mechanical properties are not like polystyrene, though it is less brittle. PHB copolymers are preferred over general purposes as the degradation rate of PHB homopolymer is high at its normal melt processing temperature. PHB and its copolymers with PHV are melt processable semi-crystalline thermoplastics made by biological fermentation from renewable carbohydrate feedstocks. They represent the first example of a true biodegradable thermoplastic produced via a biotechnology process. No toxic by-products are known to result from PHB or PHV.

PHBH

Poly-hydroxybutyrate-co-polyhydroxyhexanoates (PHBHs) resins are one of the newest type of naturally produced biodegradable polyesters. The PHBH resin is derived from carbon sources such as sucrose, fatty acids or molasses via a fermentation process. These are 'aliphatic-aliphatic' copolyesters, as disctint from 'aliphatic-aromatic' copolyesters. Besides being completely biodegradable, they also exhibit barrier properties similar to those exhibited by ethylene vinyl alcohol (see Section 3.1.2). Procter & Gamble Co. researched the blending of these polymers to obtain the appropriate stiffness or flexibility.

Research Scope

1. Use of degradable polymers can be increased to protect environment.
2. The properties of degradable polymers should be compared with those of conventional synthetic polymers
3. The properties of degradable polymers that are not acceptable can be improved by adding suitable additives, changing the chemical structure, incorporating functional groups etc.
4. After modifying the degradable polymer for achieving strength, the degradability should be assessed.
5. The residue from the polymer after degradation should be assessed for its harmfulness to the environment.

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Special Article

Theory Of Polymer Degradation

ABSTRACT: *Polymers are known for their versatile qualities of strength, durability, light weight, low cost etc. Today polymer industry is facing environmental problem regarding its degradability and its durability. Environmentalists object the use of plastic packaging because they are non degradable. In fact all polymers are degradable in longer or shorter period and that to without imposing any harm to the environment. There are many ambiguities regarding the term degradability. The present paper emphasizes on the term degradability, various types of degradability, various modes through which polymers tend to degrade, factors affecting the degradability and mechanism of degradability. Also the future research scope is shortly described.*

Polymers have become inevitable material for our daily routine life, quality and comfort. This is due to the versatile qualities of polymer with respect to their strength, lightness, durability, protection and low cost. Plastics are used in almost all industries and have virtually glass, paper and wood in the packaging and building industry. The other bulk industries are consumer goods, electrical/electronics, automobile agriculture, medical, pharmaceutical, aeronautical and space application and so on...

Synthetic polymers were originally developed for their durability and resistance to all forms of degradation, including biodegradation. These virtues of polymer have now become a greatest problem. It would be highly beneficial from the environmental stand point, if these films were biodegradable, decomposing almost completely under the attack of microorganism over a period of say few months or even they can break into fragments so that they do not become harmful to the environment.

DEGRADATION:

It is the process of polymer chain scission by the cleavage of bonds between the monomers in the polymer backbone. Hence degradation leads to a size reduction of the polymer chain.

DEBORAH NUMBER (D) is the measure of degradability.

D = TIME OF DEGRADATION / HUMAN LIFE TIME

Degradable polymers will have small values of D.

All polymers degrade in one way or other and hence all polymers can be considered degradable. But in practice if a polymer does not degrade within human life time is usually considered non-degradable.

TYPES OF DEGRADATION:

Polymer degradation is broadly of two types:

1. Chain degradation: Here the degradation stars from the chain ends resulting in successive release of monomer units. It is reverse of chain propagation hence can be called depolymerization.

2. Random degradation: It occurs at any random point along the polymer chain. It is reverse of polycondensation process. Here the polymer degrades to lower molecular weight fragments and practically no monomers are released. Almost all polymers undergo random degradation. The polymer chain need not carry any active site. The polymer molecules break up while degrading. Hence a sudden drop in the molecular weight occurs.

VARIOUS MODES OF POLYMER DEGRADATION:

1. Thermal degradation
2. Mechanical degradation
3. Ultrasonic wave degradation
4. High energy radiation degradation
5. Photo degradation
6. Chemical degradation
7. Bio degradation

Thermal and mechanical degradation occur during polymer processing. It is important when polymers are used for providing a mechanical function where they are subject to stress.

Ultrasonic wave and high energy radiation degradation occur when polymer is subjected to sterilization. Polymers are subjected to *uv* and g radiation during polymer processing to reduce the bacterial contamination.

Photo degradation occurs when polymers are exposed to sunlight during their outdoor service.

Chemical degradation occurs by introducing hydrolysable or oxidative functional group into the polymer backbone. The polymer chains become labile to an aqueous environment and thus, chemical degradation initiates polymer erosion. Different types of chemically degradable polymer bonds have different velocities at which they hydrolyze.

BIODEGRADABILITY implies the degradation that is mediated by a biological system. It is a mass loss of monomers, oligomers.

FACTORS AFFECTING DEGRADABILITY:

Synthetic polymers are inherently resistant to biological attack. But susceptibility to biodegradation varies and is affected by:

1. Additives
2. Plasticizers
3. The type of chemical bond
4. Water uptake
5. Crystallinity and molecular weight
6. pH
7. Copolymer composition
8. Enzymatic degradation

Special Article

Theory Of Polymer Degradation

1. ADDITIVES: Various compounding ingredients may have nutritive value for microorganisms. Hence may invite microbial attack. Most of the plasticizers, lubricants, thickening agents, starch and cellulose fillers are susceptible to microbial attack.

2. PLASTICIZERS: Plasticizers are occasionally used as processing aids in highly cross linked polymers. Plasticizers appear to function in polar, mainly by masking polar sites in the chain and there by reducing hydrogen bonding. In all polymers, plasticizer tends to force the chain apart, giving them greater freedom of movement and also reducing van Der Waals forces between the chains. There are no plasticizers that are completely free from fungal or bacterial attacks. Susceptibility of microbial attack increases as the plasticizer level increases.

3. THE TYPE OF CHEMICAL BOND: Various chemically degradable polymer bonds are: polycyanoacrylates, polyanhydrides, polyketals, polyorthoesers, polyacetals, poly (2-hydroxy-esters), poly (E-caprolactone), polyphosphazenes, polyB-Hydroxyesters, polyamino carbonates, polypeptides, polycarbonates, polyphosphate esters.

4. WATER UPTAKE: The hydrolysis of the polymer backbone requires water and can be increased by raising the concentration of either partner. The water uptake can be controlled by altering the lipophilicity of the system. Degradation rates increase when the hydrophilic component contents are increased.

5. CRYSTALLINITY AND MOLECULAR WEIGHT: Crystalline polymers degrade slower than amorphous polymers. High molecular weight causes increase in glass transition temperature. Hence leads to slower degradation. Higher molecular weight increases the chain length and hence more bonds have to be cleaved in order to generate water soluble oligomers or monomers to allow degradation.

6. pH: pH changes can modify hydrolysis rates by orders of magnitude. Also the degradation products of many degradable polymers change pH by their acid functionality.

7. COPOLYMER COMPOSITION: The presence of variety of functional groups affects degradability. e.g. A polymer built up of two monomers contains four types of bonds: **A-A, B-B, A-B and B-A.** This has some significance when these bonds have different hydrolysis rates.

8. ENZYMATIC DEGRADATION: Biodegradable polymers can be hydrolyzed passively or actively via enzymatic catalysis. The fastest process controls the overall degradation mechanism. Enzymatic degradation is mainly effective for natural polymers. However with non hydrolysable, water insoluble polymers such as PE, enzymatic degradation may occur. Experiments with microbes even PE was found to be enzymatically degradable, however at a low rate. Synthetic polymers with functional groups have higher chances of non specific enzymatic degradation. The combinations of enzymatically degradable and non degradable materials are useful in drug targeting and gene therapy.

MECHANISM OF BIODEGRADATION:

There are three mechanisms for the biodegradation.

1. Cleavage of crosslinks: It involves water soluble polymers that are crosslinked by covalent bonds to make them insoluble. Hydrolytic cleavage of either the crosslink or the backbone yields water soluble polymers or polymers fragments whose size depends on the density of the bonds being hydrolyzed.

2. Hydrolysis, Ionization or Protonation of pendent group: It involves water insoluble polymers that become soluble when pendent groups are hydrolyzed, ionized or protonated.

3. Backbone Cleavage: Here cleavage of the hydrolysable bonds in the polymer backbone produces low molecular weight water soluble fragments.

Actual biodegradation may be combination of all these three mechanism.

RESEARCH SCOPE:

1. Various modes of polymer degradation can be assessed and the quantity of degradation can be evaluated. The degradation procedure can be framed and should be reproducible.
2. Various factors affecting degradability can be evaluated in terms of their type, methods of incorporation in the base polymer, mode of degradation, concentration/ quantity, consistency towards degradation, processing ability, cost effectiveness, their impact on the environment i.e. the effect of residue and degradation fragments on the environments
3. The degree of degradation can be quantified and analytical methods can be developed.

Degradation mechanism can be established and a cost effective degradable polymer can be developed.

REFERENCES on Request

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Biodegradablity of LDPE

Tests as per ASTM G-21

In the past, observing microbial growth weight loss and change in strength helped assess biodegradability. All these indirect measurements were difficult to reproduce from laboratory to laboratory, giving rise to confusion on susceptibility towards biodegradation of a given polymer. Today, there are a number of international standards, and test methods, which have been developed specifically for biodegradability. The growth rating as per ASTM G-21 assesses the resistance of plastics to fungi and bacteria. This article explains how LDPE compounded with various plasticisers were subjected to growth rating test and the amount of growth and effect on specimen surface were observed.

G D Shah

Synthetic polymers were originally developed for their durability and resistance to all forms of degradation, including biodegradation. These virtues of polymer have now become the greatest problem. Enormous work is being carried out in the field of biodegradable polymers. A range of international standards, and test methods are developed specifically for the measurement of the degree of degradation.

Laboratory test protocols usually relate to evaluation of environmental degradation under simulated conditions to which a particular polymer will be exposed on disposal. Correlation with real world exposure is more difficult for biodegradation than photo degradation because the environment for biodegradation widely differs in microbial composition, pH, temperature, moisture, etc. Hence, it cannot be readily reproduced. In early years, the only tests to establish biodegradability were related to the microbial growth, weight loss, tensile and loss of other physical properties. All these are indirect measurements of biodegradation, which often lead to results that are difficult to reproduce from laboratory to laboratory, giving rise to confusion on the susceptibility to biodegradation of a given polymer.

Standard organisations for testing

A number of international standards and test methods have been developed specifically for biodegradability, product safety, and also for compost-derived products. The main international organisations that have established standards or testing methods are:

- American Society for Testing and Materials (ASTM) *(www.astm.org)*
- European Standardization Committee (CEN) *(www.cenorm.be)*
- International Standards Organization (ISO) *(www.iso.org)*
- Institute for Standards Research (ISR)
- German Institute for Standardization (DIN)
- Organic Reclamation and Composting Association (ORCA) (Belgium)

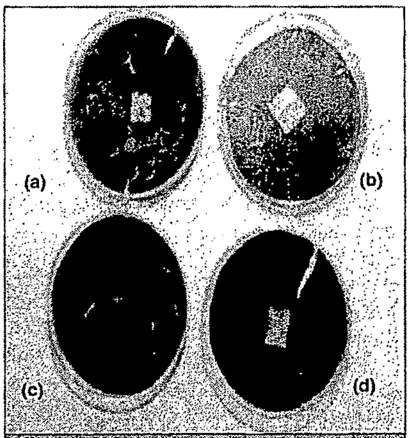

Figure 1: Growth ratings ASTM G-21 – specimens after eight weeks
(a) 25% butyl stearate, 30-35% growth white black spores and etched surface
(b) 25% cottonseed oil, 20-25% growth white black spores and etched surface
(c) 25% dioctyl phthalate, 30-35% growth white black spores and etched surface
(d) 25% epoxidised soyabean oil, 20% growth at bottom with white black spores, edges of

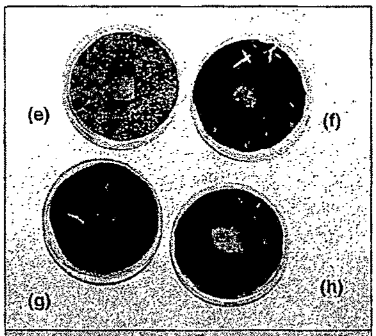

Figure 2: Growth ratings ASTM G-21 – specimens after 8 weeks
(e) 25% linseed oil, 100% growth brown fungi and etched surface
(f) 25% soyabean oil, 100% growth black fungi and etched surface
(g) 25% groundnut oil, 100% growth black fungi and sample broken to pieces and lost the handling strength
(h) 25% GPpolyester, 20-30% growth at bottom black spores and cracked surface

Growth ratings G-21-70 and GZZ-76

These tests are developed for assessing the resistance of plastics to fungal and bacterial growth. Fungi like aspergillus niger, pennicillium at 28-30°C temperature at 85 per cent RH for 21 days are used. Bacteria like pseudomonas aeruginosa incubated at 35-57°C for minimum 21 days are used. After suitable time the growth is assessed in terms of percentage surface covered. The test gives quick results. It is easy to do and gives indication of biodegradation. But it is not conclusive for biodegradation of polymers.

Experimental work

LDPE having the highest market for carry bags was selected as the base polymer. Amongst the most susceptible plasticisers, the following eight plasticisers were selected on the basis of availability and cost which is comparable with LDPE: butyl stearate, cottonseed oil, dioctyl phthalate, epoxidised soyabeen oil, linseed oil, soyabeen oil, groundnut oil and general purpose polyester.

Ten samples from each plasticiser were prepared with varying amount of plasticiser. These 80 samples were tested for biodegradability with six different organisms: pseudomonas aeruginosa, staphylococcus aureus, E-coli, aspergillus niger, penicillium and mixed culture of these microorganisms.

The specimens were subjected to screening of biodegradation of specimen in open air for one month and were under agitation for eight weeks. Eight samples with the highest concentration were selected as reference specimen. Sabouraud dextrose Himedia (MO63) agar plates were prepared overnight. The medium from the screening test was collected and mixed in the beaker. Eight samples were dipped in the mixed medium and placed on eight different agar plates.

The growth of microorganisms was observed periodically and photographs were taken for reference. After eight weeks, specimens were cleaned off the microorganisms and were visually inspected for physical changes. The microscopic view of the fungal growth and the degraded specimen were taken after eight weeks.

Results

While specimens containing linseed oil, soyabeen oil and groundnut oil showed the highest susceptibility towards biodegradation, the specimen containing butyl stearate showed moderate susceptibility towards biodegradation. The specimen containing groundnut oil showed total degradation within eight weeks, thereby proving that it was susceptible towards biodegradability. These results were confirmed by further experimentation. Hence, the commercial production of LDPE films with groundnut oil, as plasticiser should be tried.

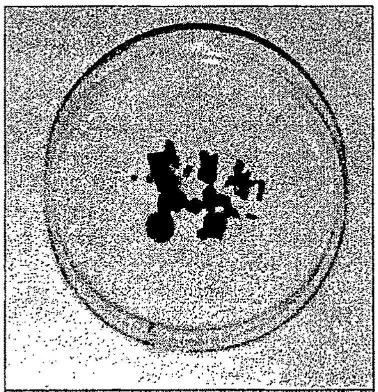

Figure 3: Degraded specimen with 25% groundnut oil

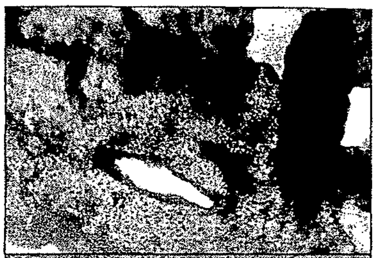

Figure 4: Microscopic view of degraded specimen with 25% groundnut oil

Inference

The basic principle of the experiment is that when a plasticiser is included in the plastic composition, it improves the extensibility of the plastics melt by way of sliding the polymer chains over each other. This sliding of chains in turn reduces the overall tensile strength of the plastic by the way of reducing the binding forces between the two adjacent chains. When these binding forces between the chains are reduced, it will be easier for the microorganism to attack on the weakened, individual chains and get nutrition for growth. Thus, degradation can be continued. The initial nutrition is obtained from the plasticiser, which exudes from the plastics specimen.

The plasticiser when exudes out of the polymeric chains, leaves space between the chains. This in turn increases the distance between the chains, thus further weakening the binding forces between the chains.

Future research scope

Some of the other test methods that could be used for assessing biodegradability include:

- Screening of biodegradation of specimen in open air
- Screening of biodegradation of specimen under agitation
- Colony growth profile on specimen in broth (liquid) medium
- Soil burial test

Further, individual microorganisms can be separated and their biodegradability

Figure 5: Microscopic view of fungal growth on degraded specimen with 25% groundnut oil

can be checked individually. New micro flora can also be developed by growing adopted microorganism in the soil nutrition by the plastic specimen. This microorganism can further be developed individually and is characterised by their ability and the rate of biodegradability of the plastic films.

The film thickness, plasticiser concentration, commercial production and cost effectiveness can be optimised. Biodegradability of other plastic material like PP, HDPE, GPPS, LLDPE, HMHDPE, etc, can be tested using the same plasticisers, ie, butyl stearate, soyabeen oil, linseed oil, groundnut oil, etc.

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MPP

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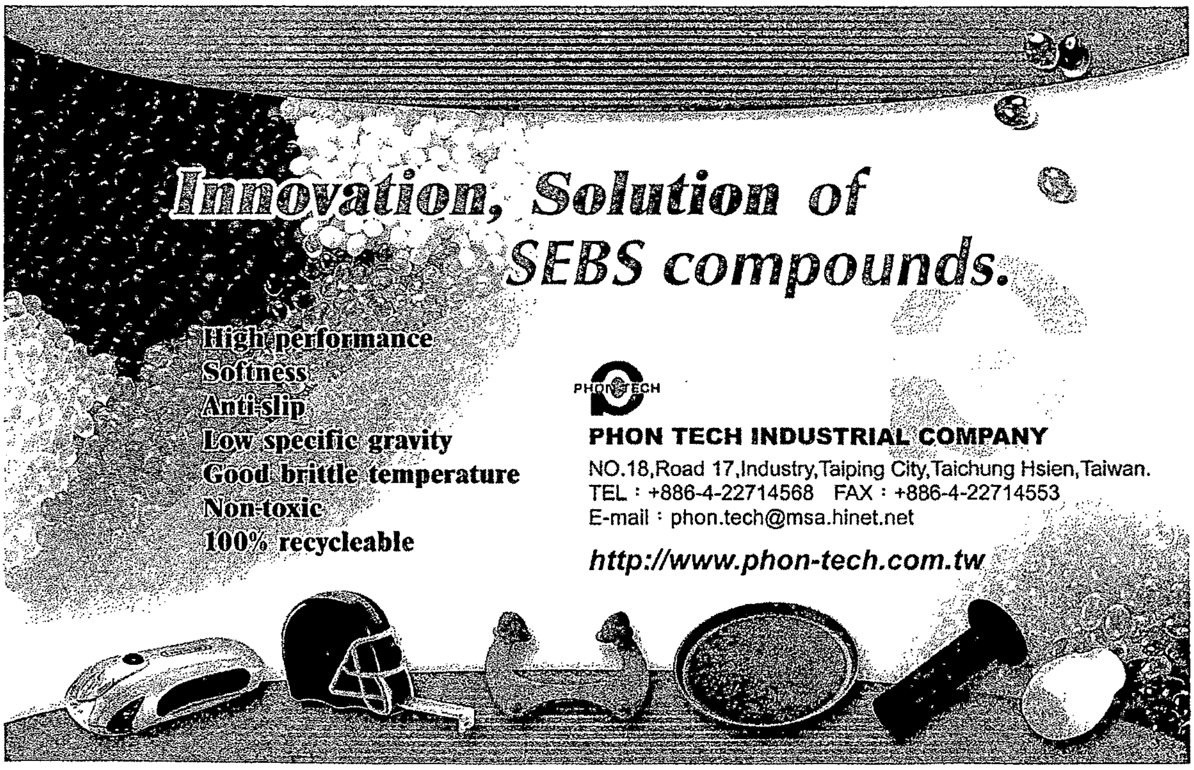

Use Plastics - Save Environment

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TODAY the mother earth is facing many environmental problems like - Global warming/ Green house effect; Thinning of the Ozone layer; Air pollution; Water pollution; Land pollution; Noise pollution; Scarcity of fuel; Scarcity of minerals; Scarcity of electricity; Scarcity of drinking water; Scarcity of conventional energy source and Eradication of wild life.

Being the children of mother earth it is our moral duty to save our mother from these problems and save her from subsequent problems of:

Flood, Famine, Earthquake and Tsunami

To overcome such environmental problems we can think of Plastics as the non-conventional material over conventional materials like:

1. Wood
2. Asbestos
3. Cotton
4. Paper
5. Iron
6. Aluminum
7. Leather
8. Silk
9. Elephant tusk
10. Pearl
11. Natural stones
12. Marbles

The non-conventional energy and material sources are considered as an option of the conventional energy and mineral resources. If plastics are considered as an option for the conventional materials like wood, metal, marble, leather, silk, cotton, jute etc. it will not only save our resources but will also save energy and our environment by the way of saving our forests, water, minerals and wild life.

Save forests/trees

Global warming/ Green house effect, Thinning of the Ozone layer and Air pollution is caused due to continuous reduction of the forest area and cutting the existing trees. To save our environment we observe WORLD ENVIRONMENT DAY, WORLD FOREST DAY and VAN MAHOTSAV. On such occasions at least one should think of the causes of reduction of trees.

Wood is being consumed mainly by: Building and construction industry; Ship building, Rail tracks, Furniture Industry, Paper Industry, Packaging, Household items and Toys.

In a residential premises of @100sq.m. approximately wood from one tree is consumed for the doors, windows etc. For furniture, and other ancillary items from wood, approximately wood from five trees is likely to be consumed. Thus if we replace wood with plastics, even for 1,00,000 of residential premises of 100 sq.m. we can save 5,00,000 trees. If such adoption of plastics takes place only in building industry, millions of trees can be saved. In India @ 55% of agricultural land is reserved for the plantation of timber wood. If the use of wood in building construction is reduced, this land can be availed for the plantation of grains, vegetables, fruits etc. Thus we can resolve our food scarcity problems to some extent. Plastic building products have several distinct advantages over traditional exterior building materials. One advantage to the consumer is that plastic building materials typically require less maintenance than other traditional materials. Unlike wood, plastics do not swell with moisture absorption, do not need to be repainted, and do not

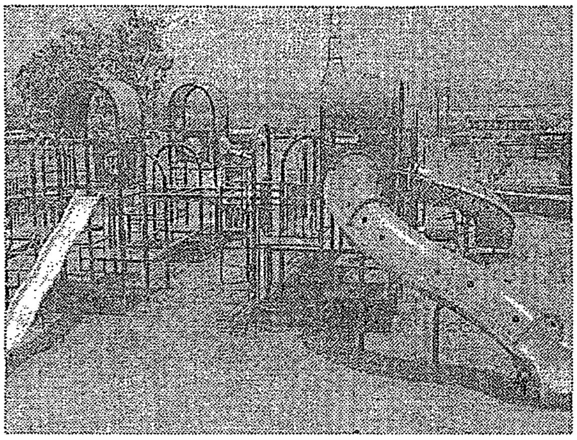

FIG.1 : PLAY GROUND EQUIPMENTS

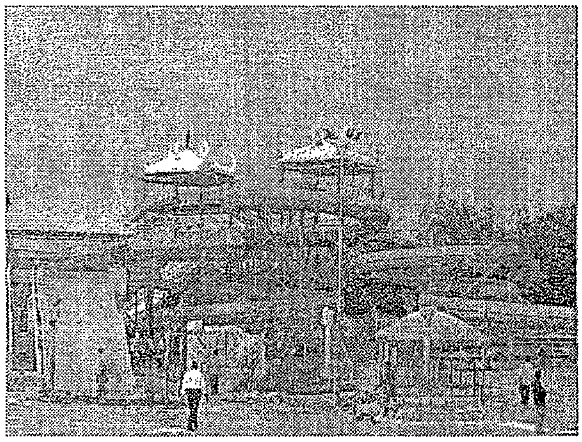

FIG. 2 : WATER PARK SLIDES FROM FRP

succumb to rotting or insect infestation. Compared to metal, plastics will not dent or rust, scratches can be buffed out and finished parts never have to be repainted. For wood in packaging an estimate indicates that if only 2% of the wooden boxes are replaced by plastic @ 1,200 ha of forests involving 1, 10,000 trees can be saved. Paper industry also utilizes major wood from the forests. Also it creates much of water pollution. If artificial cotton fibers are manufactured from plastics we can utilize this agricultural land for growing food products. The use of asbestos causes the health problem. The asbestos workers have developed statistically high incidences of mesothelioma and lung cancer and it is essential that appropriate precautions be implemented when processing the material.

Table I: Typical fabric characteristic

Property	Cotton	Polyamide	Polyester	Teflon
Tensile strength	Medium	Excellent	High	Medium
Elongation	Low	Medium	Medium	Medium
Electrical insulation	Fair	Very good	Very good	Excellent
Resistance to aging	Good	Good	Good	Excellent
Resistance to moisture	Fair	Very good	Excellent	Excellent
Resistance to heat degradation	Good	Very good	Excellent	Excellent
Resistance to mildew	Poor to fair	Good	Good	Excellent
Resistance to strong acid	Poor	Poor	Fair to good	Excellent
Resistance to weak acid	Poor	Fair	Good	Excellent
Resistance to strong alkali	Excellent	Good	Fair	Excellent
Resistance to weak alkali	Excellent	Excellent	Fair to good	Excellent
Resistance to organic solvent	Excellent	Good	Good	Excellent
Resistance to flammability	Poor	Fair	Fair	Excellent
Comparative cost	Low	Moderate	Moderate	High

Save water

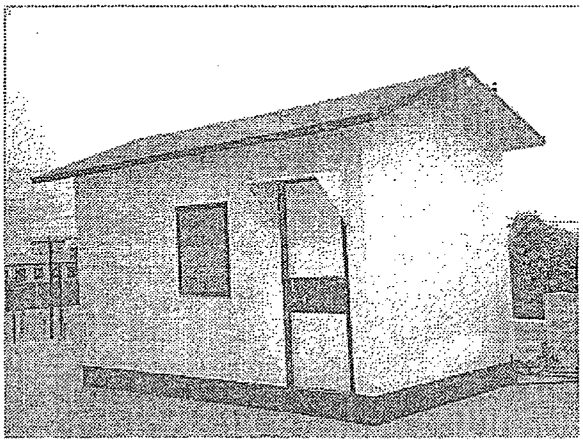

FIG. 3 : PRE-FABRICATED STRUCTURES

Water is our major natural resource. Rain is the main source of water on earth. Out of total rain some part gets evaporated in environment, some part is absorbed by land and the major part gets drained into the sea. Hence we face scarcity of water in many areas. Out of 70% of water on earth, only 23% can be used as drinking water. Out of this 23%, 84% is utilized in agriculture/irrigation. If we use drip irrigation system, mulch film technique, plastics films in green house, plastics nets in horticulture, heavy duty flexible membrane lines for canal lining to prevent water seepage, etc. all these will help saving in water and increase the productivity of crops by way of reduction of weed growth, direct supply of fertilizers to the roots of plant, and less evaporation of water. Water is also consumed in building and construction for curing the RCC structures and other miscellaneous needs. This can be reduced by covering the building by plastics film to reduce evaporation of water.

It will be also helpful by way of the reduction in frequency of watering the building. The uniformity and consistency of curing can also be observed.

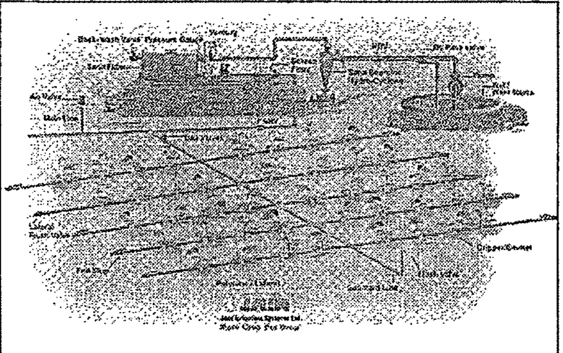

FIG. 4 : DRIP IRRIGATION SYSTEM

Save energy

The conventional resources of energy like electricity, petrol, diesel, kerosene, coal, natural gas, etc. are likely to be exhausted in coming 50 years. Hence it would be our moral duty to save these resources. Using plastics parts in automotive applications can reduce the total fuel consumption of the entire automobile vehicle range. The use of plastics parts will reduce the total weight of the automobile body without much reduction in the strength. It is estimated that 100 kg of plastics will replace 200-300 kgs of conventional materials in a typical car. This results in a 750 litres fuel consumption saving over a life span of 150,000 km.

The electric insulating property of the plastics will be useful in saving the electricity consumption in various home appliances like: Air conditioners, Refrigerators, Wire insulation, Doors and window panels, Walls and ceiling, Ovens, Cooking range etc. The light weight of plastics part will reduce the consumption of electricity in running the huge machineries. The insulated electric circuits will reduce the loss of electricity in leakage.

Also the thermal insulating property of the plastics justifies their use in various kitchen wares to save the heat energy.

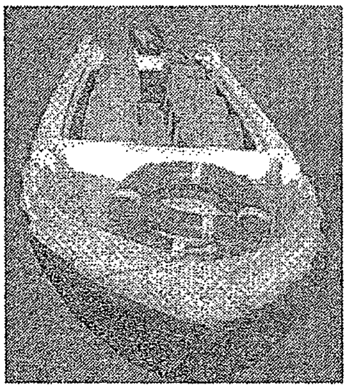

FIG. 5 : FRP BOAT

Save wild life

As per one survey there must be forests on @ 33% of total land so as to maintain the environmental balance. In India only 19.4 % of land is covered by the forests. This has resulted in reduction of the wild life. We observe WILD ANIMAL WEEK, WILD ANIMAL DAY for the rescue of the wild life. Why not we think of an alternative material for saving wild life.

1. People use elephant tusk in manufacturing various ornamental and decorative articles. For this they kill elephants. Instead if we use plastics for this purpose we can save elephants and the ornaments and decorative items can be also availed to the people at low cost.

2. We use the skin of lions, tigers, zebra, cobra, etc. for our satisfaction and thrive for fashion. The appearance and feel of the skin of lion, tiger, zebra, cobra, etc. can be obtained from plastics by applying certain processing techniques and adjusting the material recipes.

3. Wool from goat, sheep, yak, rabbit, wolf, bear, etc. is obtained for the special feel of fur. This can be achieved by using corresponding plastics fibers.

4. To manufacture a single sari from silk millions of silk worms are killed. Instead if we use the artificial silk from the corresponding plastics we can use the natural silk in various engineering applications.

5. We use leather in various applications like leather over coats, jackets, purses, wallets, foot wears, luggage, and recreational items. This has caused danger on the wild life. If we use artificial leather made from plastics, it will save the wild life and the cost of these products will also be reduced.

6. Pearl and natural stones are used in making ornaments and garments. For this we surf the sea water. This in turn imposes danger on the sea life. If we use plastics to manufacture the artificial pearl and stones we do not have to compromise with the appearance and feel. On the contrary we can get variety in colors and shape. Also the ease of fabrication and reproducibility are added advantages.

Save minerals

Many phases of human civilization are described by minerals right from the Stone Age to the Atomic Age. The use of minerals ranges from a small pin to a huge machine and space craft. We obtain minerals by mining deep in to the earth. This mining causes air, water, land and noise pollution.

Table II: Comparative study of strength of various materials

MATERIAL	% GLASS FIBRE	FLEXURAL STRENGTH psi x 10^3	TENSILE STRENGTH psi x 10^3	COMPRESSIVE STRENGTH psi x 10^3	ELONGATION %
SMC	15-30	18-30	8-20	15-30	0.3-1.5
ACETAL	20-40	15-28	9-18	11-17	2
NYLON	6-60	7-50	13-33	13-24	2-10
PC	20-40	17-30	12-25	14-24	2
PE	10-40	7-12	6.5-11	4-8	1.5-3.5
PP	20-40	7-11	5.5-10.5	6-8	1-3
PS	20-35	10-17	10-15	13.5-19	1-1.4
ABS	20-40	23-26	11-16	12-22	3-3.4
PVC	15-35	20-25	14-18	13.4-16.8	2-4
ALUMINUM DIE CASTING	-	8-26	8-29	9	6-8
ALUMINUM WROUGHT	-	20	6-27	-	30-40
STAINLESS STEEL	-	30-35	30-35	30	50-60
LOW CARBON STEEL	-	28	29-33	28	38-39

Over and above since the mineral are extracted from various layers of land, vacuum has been created between the upper layer of the land and the deeper most layer of the land. This in turn may be one of the causes of the natural disasters like earthquakes, floods, Tsunami, etc. Also this extraction of minerals has caused its scarcity too. Hence one has to think for the alternative non conventional material. Plastics can replace steel, aluminum, glass, marble etc. with the comparable strength at lower costs of manufacturing and maintenance.

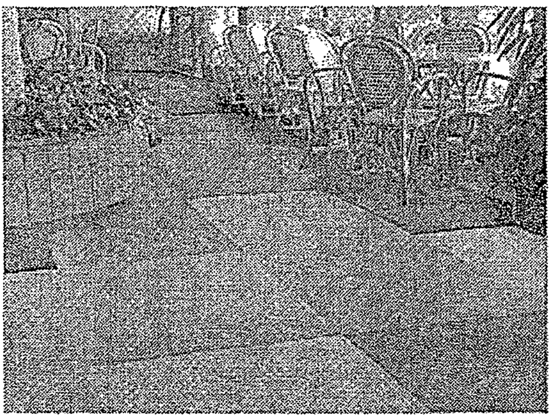

FIG. 6 : ARTIFICIAL MARBLE FLOORING

Summary

Plastic is the material of the 21st century. It offers unlimited possibilities. We can do anything with plastic. The entire world could be made of plastic. There are even heart implants made of plastic: we are actually walking around with a piece of plastic inside us. It is remarkable how much in our environment is made of this material without our even noticing it. And it is amazing that there are still so many people who are skeptical towards plastic even though they use it every day. It is suggested that the environmentalists should focus on the diminishing natural resources and should put their efforts in saving these scarce natural resources.

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Mrs. G. D. Shah is Incharge, Head of Plastics Engineering Department since May 2002 at the Government Polytechnic Ahmedabad. She completed her B.E. (Plastics Technology) in July 1989 with a First Class Distinction from Gujarat University. A "University First" at the graduation level, she has passed M.E. Chemical Engineering (Polymer Technology) with First Class from M.S. University, Baroda in Jan 2002 and has a total teaching experience of 17 years. Her major area of research is on biodegradable polymer microfilms, the subject on which she has worked for 6 years. Her other areas of interest are product design and innovative polymer materials. A Life member of ISTE and IIChE, she is also the Ladies representative of Polytechnic Adhyapak Mandal, Gujarat State.

Testing Protocols For Biodegradation

6. Standard Test Method for Determining the Aerobic Biodegradability of Degradable Plastics by Specific Microorganisms D5247-92

This test method describes the procedures required to carry out a pure-culture study for evaluating the biodegradation of degradable plastics in submerged culture under aerobic conditions. Degradation will be evaluated by weight loss, tensile strength loss, percent-elongation loss and changes in molecular-weight distribution.

7. Standard Test Method for Determining Weight Loss From Plastic Materials Exposed to Simulated Municipal Solid-Waste (MSW) Aerobic Compost Environment D6003-96

This test method determines the degree and rate of aerobic biodegradation of plastic materials exposed to a controlled composting environment. Aerobic composting takes place in an environment where temperature, aeration, and humidity are closely monitored and controlled.Biodegradability of the plastic is assessed by determining the amount of weight loss from samples exposed to a biologically active compost relative to the weight loss from samples exposed to a "poisoned" control.

8. Standard Practice for Exposing Plastics to a Simulated Active Landfill Environment D5525-94a

The plastic is exposed to a specific test environment. The test environment is a laboratory-scale reactor that simulates a landfill with enhanced biological activity. Biological activity is enhanced by adding moisture, recirculating leachate, and heating to 35°C. Plastic exposure occurs in the presence of a media undergoing anaerobic degradation. The standard media used in the practice simulates a municipal solid-waste stream.

9. Standard Test Method for Determining Anaerobic biodegradation of Plastic Materials under Accelerated Landfill Conditions WK9579 Revision of D5526-94(2002)

Landfills begin as aerobic environments and transform into anaerobic environments over time and as they are filled. Hence a need to have a biodegradation standard for both environments. Also, there is a need to measure the degree of degradation / disintegration in the aerobic phase over time which will correlate with the packing of landfill sites and volume availability

10. New Standard Specification for Determining the Biodegradability of Plastics. Under Accelerated Anaerobic Conditions WK10726

The extent of biodegradation of plastics under anaerobic conditions is determined. The degradation of these materials should not introduce any hazardous chemicals into the landfills that may pose a risk in the future.

11. GROWTH RATINGS G-21-70 AND GZZ-76

These tests are developed for assessing the resistance of plastics to fungal and bacterial growth. Fungi like aspergillus niger ,pennicillium at 28-30°C temperature at 85% RH for 21 days is used. Bacteria like pseudomonas aeruginosa incubated at 35-57°C for minimum 21 days are used. After suitable time the growth is assessed in terms of % surface covered. The test gives quick results. It is easy to do and give indication of biodegradation. But it is not conclusive for biodegradation of polymer.

INTERNATIONAL STANDARDS ORGANIZATION (ISO) (WWW.ISO.ORG): (4, 6, 7, 8, 10, 13, 14)

Three International Standards Organization (ISO) standards have set the criteria by which

European biodegradable plastics are currently assessed. These are:

i. ISO 14855 (aerobic biodegradation under controlled conditions);

ii. ISO 14852 (aerobic biodegradation in aqueous environments); and

iii. ISO 15985 (anaerobic biodegradation in a high solids sewerage environment).

ISO 14855 is a controlled aerobic composting test, and ISO 14851 and ISO 14852 are biodegradability tests specifically designed for polymeric materials. An important part of assessing biodegradable plastics is testing for disintegration in the form in which it will be ultimately used. Either a controlled pilot-scale test or a test in a full-scale aerobic composting treatment facility can be used. Due to the nature and conditions of such disintegration tests, the tests cannot differentiate between biodegradation and abiotic disintegration, but instead demonstrates that sufficient disintegration of the test materials has been achieved within the specified testing time.

ISO 846 (1978):

It specifies the use of a mixture five strains of fungi over a period of at least 28 days at 30 ±2°C and 95-100% RH.

▸▸▸▸▸▸

Note Worthy

Testing Protocols For Biodegradation

The results of attack are measured by visual examination for growth.

Method A is used to determine the ability of plastics to act as the carbon and nitrogen source for the growth of microorganisms.

Method B is used to determine the fungi toxic properties of plastics.

COMPOST TOXICITY TESTS (4, 6, 7, 8, 10, 13, 14)

For a comprehensive assessment of toxicity associated with compost applications, plastics can be tested on both plant and animal species. A number of polyester types were tested including a plasticized cellulose acetate, an aliphatic polyester, polyhydroxybutyrate-co-hydroxyvalerate and polycaprolactone. Cell culture medium with serum was used as the extraction medium.

PLANT PHYTOTOXICITY TESTING (4, 6, 7, 8, 10, 13, 14)

While a product may not negatively impact plant growth in the short term, over time it could become phytotoxic due to the build-up of inorganic materials, which could potentially lead to a reduction in soil productivity. For this reason some manufacturers use plant phytotoxicity testing on the finished compost that contains degraded polymers. Phytotoxicity testing can be conducted on two classes of flowering plants. These are monocots (plants with one seed leaf) and dicots (plants with two seed leaf). Representatives from both of these classes are typically used in toxicity testing - summer barley to represent monocots and cress to represent dicots. Tests involve measuring the yield of both of these plants obtained from the test compost and from control compost.

ANIMAL TOXICITY TEST (4, 6, 7, 8, 10, 13, 14)

Animal testing is generally carried out using earthworms (as representative soil dwelling organisms) and Daphnia (as representative aquatic organisms). Earthworms are very sensitive to toxicants. Since earthworm feeds on soil, they are suitable for testing the toxicity of compost. In the acute toxicity test, earthworms are exposed to high concentrations of the test material for short periods of time. Earthworms are exposed to soil and compost in varying amounts. Following 14 days of exposure, the number of surviving earthworms is counted and weighed and the percent survival rate is calculated. The earthworms are exposed to several mixture ratios of compost and soil mixtures.

Compost worms are used for testing the toxicity of biodegradable plastic residues. These worms are very sensitive to metals such as tin, zinc, and heavy metals and high acidity. For this test worms are cleaned and accurately weighed at intervals over 28 days. The compost worm toxicity test is considered to be an accurate method. The toxicity test can establish whether degradation products present in liquids pose any problem to surface water bodies. In the test, Daphnia are placed in test solutions for 24 hours. After exposure the number of surviving organisms is counted and the percent mortality is calculated.

SOIL BURIAL TEST BS 4618 SEC.4.5 1974 (4, 6, 7, 8, 10, 13, 14)

Soil burial is a traditional way to test samples for degradation because of its similarity to actual conditions of waste disposal. It lacks reproducibility because of the difficulties in controlling climatic factors and the population of various biological systems that are involved. Generally the samples are buried in soil for periods of up to two years. At the end of the resting period, changes in properties like loss in weight, mechanical strength, shape etc. are studied. It provides qualitative indication of biodegradation.

DIFFERENCE BETWEEN STANDARDS FOR BIODEGRADATION (13, 14)

The main point of differentiation between the various international standards is the percentage of biodegradation required for compliance. This is an important issue that is under discussion at ISO level. The compliance requirements for the key standards are shown in Table 6.1.

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Recycling of plastics - A solution to waste management

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ABSTRACT

Plastics consumption has grown at a tremendous rate over the past two or three decades. In the 'consumer' societies scarce petroleum resources are used for producing an enormous variety of plastics for an even wider variety of products. Many of the applications are for products with a life-cycle of less than one year and then the vast majority of these plastics are discarded. In most instances reclamation of this plastic waste is simply not economically viable. In industry (the automotive industry for example) there is a growing move towards reuse and reprocessing of plastics for economic, as well as environmental reasons, with many praiseworthy examples of companies developing technologies and strategies for recycling of plastics. Plastics are made from a non-renewable resource and it is generally non-biodegradable (or the biodegradation process is very slow). Hence plastics litter is often the most objectionable kind of litter and will be visible for weeks or months, and waste will sit in landfill sites for years without degrading. There is a much wider scope for recycling in developing countries like India.

PLASTICS are unique, remarkable versatile material having fantastic properties to fulfill the need of our modern society. The plastic age arrived in 1868 with the invention of "CELLULOID" by Alexander Park to replace billiard ball previously made of ivory. In 1909 Leo Backeland derived "BACKELITE" i.e. phenol formaldehyde - a thermo set material. The other plastics like PP, PS, PC, PVC, NYLON, TEFLON POLYSULFON, and other engineering plastics were derived in the last 100 years.

Virtually every known plastics material is used in some aspect of packaging. After using packaged item the plastics wrapper, bag, or container is merely a waste. During plastics processing also some portion of material is in the form of waste along with the finished products. But such fresh waste is reprocessed or converted in to scrap form and is reused along with virgin materials up to 15%. But the huge amount of waste generated by industry and the consumer can not be ignored. Plastics waste becomes nuisance for human beings. Environmentalists and regulatory authority are thinking that plastics are not environment friendly and cause health hazards.

This is not true

Actually implementation of eco friendly waste disposal management system should be developed to solve this problem. Plastics waste itself is not at all dangerous to human being but the unscientific manner of waste disposal creates the danger.

Waste disposal management systems

To reduce the problem of ecological imbalance, due attention must be given to waste managements systems like:

1. Recycling
2. Combustion or incineration (5%)
3. Land filling (40%)
4. Source reduction
5. Repairs
6. Reuse
7. Degradation of polymers
8. Use as fillers

Types of waste

1. Waste products - defective products
2. Industrial waste

3. Post consumer waste- packaging films, damaged moldings etc.
4. Nuisance waste- thermo set waste
5. Scrap waste- feed system, flash, finishing scrap etc.

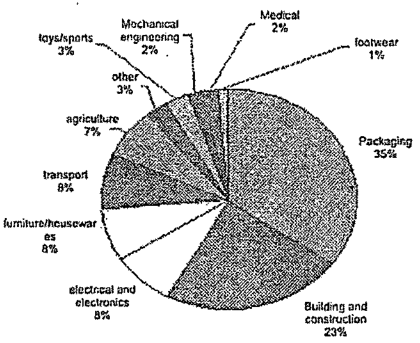

Fig. 1 : Use of plastics in various sectors

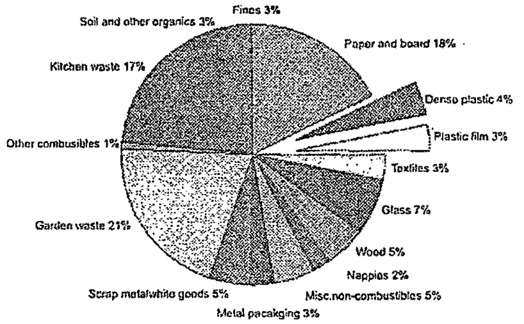

Fig. 2 : Plastics waste through various industries

Definitions

Regrind Material: The plastics scrap obtained from grinding machine in form of coarse powder is known as regrind material.

Reprocess Material: The regrind material obtained in the form of pellets from granulation line of extruder is known as reprocess material.

Recycle Material : The regrind material compounded with suitable additives so that the quality of reprocess material approaches to that of virgin material.

Process of recycling

The manufacture of recycle material involves five steps:

1. Separation from municipal solid waste
2. Grinding the plastics waste material
3. Reprocessing material
4. Testing for quality reduction
5. Compounding to attain virgin quality

Separation from municipal solid waste

The municipal waste is reduced in size mechanically by tension, compression, shear using crushers, shears, chippers, drum pulverizers, disc mills, pulpers and hammer mills.

After making small particles each individual particles are separated by:

1. density - floating in water
2. magnet - ferrous particles
3. manual - glass, paper etc.
4. gravity - fluidized bed separation
5. electrostatic - charged particles by attraction to a charged roll
6. color - different colored particles
7. air separation - paper and light weight material by blowing air
8. heat separation - hot roll or doctor blade
9. solvent extraction - dissolution in solvent

Grinding

The plastics waste material is obtained in various forms viz. the feed system, flash, film, molded product etc. all these forms must be sorted out and possibly cleaned. These materials are now cut to suitable size so that they can be fed to the grinding machine. The regrind material obtained from various forms of scrap is collected separately.

Reprocessing

The regrind material is then fed to the hopper of an extruder which is previously prepared for processing. While using the film material as regrind material, care should be taken for positive feeding because the film has high bulk density.

After the material is melted to the required melt temperature, the material extruded from the granulation die of the extruder in the form of long, continuous strands. These strands after cooling are cut to the required pellet size. The pellet size i.e. length and diameter can be varied to some extent by varying the take off speed of the cutter.

Testing

The reprocess material always involves quality reduction. The reason is:

The processing of plastics involve the melting of material to required processing temperature and then cooling this melt so as to obtain required shape. While melting the material, the heat is imparted to that material and while cooling the material, the heat is extracted from the material.

While heating the material the bond in the polymer chain expand and the molecular distance is increased. While cooling the bonds contract and the molecular distance is reduced. While reprocessing these steps are repeated. Due to these expansion and contraction, some of the heat energy is absorbed by the bonds so the bond strength is reduced. Due to this reduction this reduction in bond strength, now less energy is required to break this bond i.e. the strength of the material or resistance towards load is reduced. Also during these heating and cooling process, some of the bonds break. Thus there is reduction in molecular weight and corresponding strength.

This reduction is tested by measuring melt flow index of the reprocess material, because MFI is inversely proportional to the molecular weight of the material and corresponding melt viscosity.

Table: Effect of molecular structure on various properties of plastics material

Sr.	Property	Linear chain Polymer	Branched chain Polymer
1	Density	More	Less
2	Permeability	Less	More
3	Tensile strength	More	Less
4	% elongation	Less	More
5	Stiffness	More	Less
6	Crystallinity	More	Less
7	HDT	Less	More
8	Softening temperature	Less	More
9	Hardness	More	Less
10	Creep resistance	More	Less
11	Flow ability	Less	More
12	Compressibility	Less	More
13	Impact strength	Less	More

Compounding

This step involves the addition of suitable additives to improve particular quality of the material. The material and additives are then mixed into a homogeneous mass with the help of suitable compounding methods. The selection of compounding method depends upon the additives added and the mixing quality required.

Modes of recycling

Depending on the products obtained after recycling it can be explained as:

1. Primary recycling
2. Secondary recycling
3. Tertiary recycling
4. Quaternary recycling

Primary Recycling

It is the processing of scrap plastics into the same or similar type of product from which it has been generated using standard plastics processing methods.

Uniform, uncontaminated plastics waste reprocessed directly after scrapping particularly thermoplastic waste.

Plastics waste is ground to a particle size close to that of virgin material. The size reduction is done in scrapping machine consisting of a hopper, cutting chamber (rotor knives), fixed and rotating cutters, screen and drive. The knife arrangement may be parallel, slanted, V type, etc. Counter rotating rotors or two step rotors are also designed for scrapping. Cryogenic grinders are available for difficult material. For film type material waste plunger type or screw type stuffer is used.

Secondary Recycling

Secondary recycling utilizes plastics waste unsuitable for direct reprocessing using standard plastics processing equipments.

Plastics waste feedstock from:

1. Post consumer plastics waste recovered from municipal refuse.
2. Post consumer plastics waste obtained from returnable packages (milk pouches, jars, soft drink bottles etc.)
3. Industrial plastics waste consisting of a single type of plastics material.

Reverser machines are used to manufacture products from contaminated and/or mixed thermoplastic waste. It can employ as feed stock such as PVC, PE, Nylon and used bottles and drums. It can handle contaminated scrap- pieces of copper, sand, glass etc. Waste plastics are pulverized in a crusher, dried and conveyed to large extruder and from extruder the material is delivered to accumulator; from accumulator a vertical screw plunger discharges the material into the mould. Final products can be formed by intrusion (flow molding), compression molding or extrusion.

Tertiary recycling

It is the pyrolysis of post consumer waste. In this process the physical and chemical decomposition of organic materials caused by heating in an oxygen free atmosphere. This process is used for manufacturing charcoal, acetic acid and turpentine.

Pyrolysis is an endothermic reaction and heat must be supplied to distill off the volatile components.

Primary reactions

Organic material → gases + liquid + char

Secondary reactions

$CO_2 + H_2O \rightarrow CO_2 + H_2 + \Delta$

$C + H_2O \rightarrow CO + H_2 + \Delta$

$C + CO_2 \rightarrow 2CO + H_2 + \Delta$

$C + O_2 \rightarrow CO_2 + \Delta$

$C + 2H_2 \rightarrow CH_4 + \Delta$

As shown, the products of pyrolysis of solid waste are in the form of gases, liquids and char.

The solid residue from the process was in the form of a light weight, flocky char, which could be coarsely sieved to remove extraneous materials such as bottle caps and lids.

The liquid portion of the pyrolysis products consists of tar, light oils and liquor.

Quaternary recycling: (Energy from plastics waste)

Incineration of refuse is done to reduce combustible waste to inert residue by controlled high temperature combustion. The main reason for incineration is reduction in the volume of waste. Incineration is capable of reducing the weight of refuse by 80% and the volume by over 90%. The residue from the refuse is inert and may be disposed off in land fill.

Energy recovery

1. By burning refuse in steam generating incinerators to generate electricity.
2. Pouring refuse in existing heat exchangers as a fuel in power boilers.
3. Pyrolysis of refuse can be employed to produce a transportable fuel.
4. Refuse can be converted to heavy oil by hydrogenation by heating under pressure in the presence of carbon monoxide and steam.
5. In anaerobic digestion the organic portion of the refuse is decomposed in the absence of oxygen. Methane produced has the potential of being used as a natural gas substitute.

At present time, burning refuse in steam generating incinerators and its use as supplemental fuel are the most advanced waste energy utilization technologies.

An incinerator consists of:

1. Scale	→	To measure the weight of feed
2. Storage pit	→	To collect feed stock
3. Cranes	→	To handle waste from storage t o furnace
4. Charging/ Feeding mechanism / Hopper	→	For furnace
5. Furnace	→	Where combustion occurs
6. Boilers	→	For generating steam
7. Steam turbines	→	To convert heat energy to mechanical energy
8. Generators	→	To convert mech. energy to electrical energy

Lastly, the environmental attack on the plastics industry is not justified because of the small contribution of solid waste (2-4% only). Also the large portion of waste generated by industry is reprocessed or recycled in the industry it self.

Not all plastics waste can be easily recycled. At present a considerable portion of plastics waste is still being disposed off without the recovery of cost incurred in production. However rising material and energy costs, govt. regulations and awareness of the consumer exert a pressure on the industry to change the situation. New separation techniques, incinerators and technology will make more recovery of energy and chemically possible scientific waste disposal management.

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Waste management of plastics material

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THE World Environment Day is observed on 5th June every year, to conserve our environment. Plastic waste remains one of the biggest headaches globally. Piles of plastic waste have become a common site in towns, and the menace is rapidly spreading to the countryside. Plastics have become an indispensable part of our daily life. But repeated reprocessing of plastic waste, and its disposal creates environmental problems, pose health hazards, although plastics pose a hazard to the environment because they do not decay, plastics are preferred because they are cheap and versatile.

Health impacts of solid waste

The unhygienic use and disposal of plastics and its effects on human health has become a matter of concern. Colored plastics are harmful as their pigment contains heavy metals that are highly toxic. Some of the harmful metals found in plastics are copper, lead, chromium, cobalt, selenium, and cadmium. In most industrialized countries, colour plastics have been legally banned. Until recently no legislation was framed to deal specifically with issues connected with plastic waste management. The Government of Himachal Pradesh was one of the earliest to introduce legislation prohibiting the throwing or disposing of plastic articles in public places. The Union Ministry of Environment and Forests has recently notified the "Recycled Plastic Manufacture and Usage Rules, 1999". These rules require that carry bags or containers used for purposes of storing shall be made of virgin plastic and be in natural shade or white. These items when made of recycled plastic and used for purposes other than storing and packaging of foodstuffs shall use pigments and colorants as per Indian Standards. Recycling of plastics shall also be undertaken strictly in accordance with specifications prescribed by the Bureau of Indian Standards, and shall carry a mark that the product is manufactured out of recycled plastic. The thickness of carry bags shall not be less than 20 microns. Finally and most importantly, Rule 4 prohibits all vendors from using carry bags or containers made out of recycled plastics for storing, carrying, dispensing or packaging of foodstuffs. In other words all vendors are required to use carry bags and containers manufactured to specifications prescribed in the 1999 Rules.

Sorting of wastes

Waste is separated into the following categories:

1. kitchen wastes
2. paper and cardboard
3. glass
4. aluminium
5. other metals
6. oils, fuels, other liquids
7. wood
8. batteries
9. other materials, plastics, construction materials and obsolete items

Preventive measures

Proper methods of waste disposal have to be undertaken to ensure that it does not affect the environment around the area or cause health hazards to the people living there. At the household-level proper segregation of waste has to be done and it should be ensured that all organic matter is kept aside for composting, which is undoubtedly the best method for the correct disposal of this segment of the waste. In fact, the organic part of the waste that is generated decomposes more easily, attracts insects and causes disease. Organic waste can be composted and then used as a fertilizer.

Waste disposal options

Plastics material offer many waste disposal options because they are usually solid, handleable materials. They are recoverable in most cases after use for several disposal options. This includes:

1. Incineration
2. Recycling
3. Land fill
4. Composting
5. Reuse
6. Source of energy
7. Reclamation

Incineration

Qualified staff operate high-temperature two-chamber incinerators at all stations. Incinerator ash and residues are returned to disposal. Kitchen and medical waste, low grade paper and cardboard, contaminated low density polythene (rubbish bags) and solid human waste from field camps are incinerated. All fats and oils, plastics (including polyurethane foam, polystyrene), large quantities of timber boxing and out-of-date food are returned for waste management.

Disadvantages of incineration

1. Incineration destroys valuable resources.
2. Burning fossil fuels like coal, oil and gas is causing increasing levels of carbon dioxide in our atmosphere, leading to climate change. Incineration contributes to climate change, because when materials are burnt more fossil fuel energy is used to replace them through mining, manufacturing, and transportation around the world. Energy from burning waste is not renewable.
3. Incinerators need a steady stream of waste to keep them going. This means there is no incentive to reduce waste or recycle it.
4. Incineration causes pollution from air emissions and toxic ash.
5. Incineration is worse for climate change than recycling because new products have to be made to replace those destroyed.
6. Incineration does not provide the thousands of new job opportunities that recycling does.

Recycling

Many items are re-used on station, e.g. packing materials such as cardboard boxes and plastic sheeting, packing crate timber, 200 L drums either with the lid part opened (for metal waste, glass or incinerator ash) or intact for returning chemical waste (e.g. photographic chemicals). Official photography on stations is now substantially electronic (i.e. no wet processing). All stations sort wastes as indicated above for disposal to recyclers. Recycling is one of the most immediate and effective ways to protect the environment. By recycling instead of producing goods from raw materials, substantial amounts of energy and raw materials are saved. 40% of local authorities now provide facilities for recycling plastics, with a quarter of these involved in doorstep collection schemes which are the most successful in recovering plastic waste. The six most common types of plastic can all easily be recycled and have a much higher value than most recyclable materials. As the volume of recycled material increases markets will expand, making the material more attractive to industry and the benefits of recycling more apparent. Recycling and waste minimization businesses could employ over 100,000 more people than the landfill and incinerator businesses would make redundant. Hence we can:

- Buy products made of recycled plastic wherever possible.
- Recycle plastic plants can be established.
- Set up a community scheme. The Community Recycling Network can help
- Encourage recycling in your workplace/school/church, etc.

Landfill

Friends of the Earth wants a ban on new landfill capacity until policies are in place to achieve the 60-80 per cent recycling rates achieved in other countries, because:

- Landfill waste valuable resources.
- Landfill contributes to climate change, because when materials are buried more fossil fuel energy is used to replace them through mining, manufacturing, and transportation around the world.
- Landfill produces methane, a powerful greenhouse gas which contributes to climate change.
- Landfill creates water pollution as liquid from landfill sites leaks into our water supply.
- Landfill can lead to land contamination.
- Landfill leads to increased traffic, noise, smell, smoke, dust and litter.

Composting

Composting is predominantly biodegradation with the possibility of oxidation and hydrolysis. There is an opportunity for environmentally degradable plastics which are used in food application such as wrappers and utensils in these uses, plastics are contaminated with food residues and are suitable for composting without separation. Where recovery of current plastics is not economically feasible, viable, controllable or attractive, the plastics remain as litter and may be discarded at sea from naval vessels, may be used in farm and agricultural application such as pre emergency plant protection or in hygienic application such as diapers, hospital garments and swabs etc.

Re-use

It makes sense and it saves energy to re-use rather than recycle, but it is currently more economical for manufacturers to produce new product rather than wash and re-fill packaging. The Body Shop will re-fill plastic bottles with the same product, and many small producers across the country also do this, showing that re-use can make economic sense.

- Re-use plastic bags, or better still avoid them by using a sturdy bag that will last for years.
- Re-use pots with lids for storage rather than buying new ones.
- In the garden, re-use plastic pots for raising seedlings and cut-down plastic bottles to protect them from slugs
- Give usable goods to charity shops, or hold car boot sales for charity with any plastic items that can be re-used.
- Ask suppliers if they will take back plastic items for re-use: for example, plant pots in garden centers.
- Use refillable toner cartridges.

A source of energy

Material recovery is by no means the only way to recycle plastics. Another option is to recover their thermal content, providing an alternative source of energy. An average typical value for polymers found commonly in house hold waste is 38 mega joules per kilogram (MJ/kg), which compares favorably to the equivalent value of 31 MJ/kg for coal. This represents a valuable resource raising the overall calorific value of domestic waste which can then be recovered through controlled combustion and re-used in the form of heat and steam to power electricity generators. Successful ventures in this field include plants, such as a major incinerator, which produces steam to power an electricity turbine. Waste containing plastics can also be reprocessed to yield fuel pellets, which have the added advantage of being storable.

It is sometimes claimed that incineration of municipal waste poses an environmental problem in the shape of atmospheric pollutants. Although the potential is there, modern incineration techniques ensure that actual emission levels are kept with-in internationally accepted safety limits. In fact, several countries, such as Sweden, Germany and the Netherlands, have recently affirmed their confidence in incineration by announcing plans to expand existing capacity.

About the Author

Mrs. G. D. Shah is Incharge, Head of Plastics Engineering Department since May 2002 at the Government Polytechnic Ahmedabad. She completed her B.E. (Plastics Technology) in July 1989 with a First Class Distinction from Gujarat University. A "University First" at the graduation level, she has passed M.E. Chemical Engineering (Polymer Technology) with First Class from M.S. University, Baroda in Jan 2002 and has a total teaching experience of 17 years. Her major area of research is on biodegradable polymer microfilms, the subject on which she has worked for 6 years. Her other areas of interest are product design and innovative polymer materials. A Life member of ISTE and IIChE, she is also the Ladies representative of Polytechnic Adhyapak Mandal, Gujarat State.

Reclamation

The majority of municipal waste is still used as land fill, due to the very high cost of facilities for the sorting, separation and recycling of waste. As plastics are stable, both physically and chemically they in turn provide stability to the tips. This provides a safe and solid foundation upon which to build; thereby releasing land for development.

Conserving the environment

The plastics industry is concerned that it should take appropriate care of resources and the environment. The advantages of plastics over other raw materials are apparent from the beginning of their life-cycle. Research shows that it often takes less energy to make products in plastics, and although most plastics depend on oil, coal or gas they are responsible for only a small fraction of the national consumption of these fuels. Energy savings can be made easily with plastics because plastics are lighter, easier to store and transport. Also the developments in the recycling of plastics, there are interesting advances in the production of degradable plastics for products which need only a limited life.

The future

Plastics recycling are in the growth phase as the whole industry is still relatively young. A further development in recycling, which is being researched, is the recovery of the individual chemical components of plastics for re-use as chemicals, or for the manufacture of new plastics.

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BIODEGRADABLE LOW DENSITY POLYETHYLENE

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ABSTRACT

LDPE in its unmodified form is not biodegradable. When it is compounded with additives or plasticizers, it is affected by microorganism in various degrees. Low Density Polyethylene film grade was compounded with Butyl stearate, Cottonseed oil, Dioctyl phthalate, Epoxidized soyabeen oil, Linseed oil, Soyabeen oil, Groundnut oil and General purpose polyester plasticizers. The amount of plasticizers was varied from 5-25% (w/w).The biodegradability was evaluated with respect to amount duration and type of plasticizer. The microbial susceptibility of various plasticizers was checked. Approximation of plasticizer concentration that exhibits highest susceptibility towards microbial attack was determined. The test method employed was screening of biodegradation of specimen under agitation.

INTRODUCTION

All polymers degrade in one way or another and hence all polymers can be considered degradable. But in practice if a polymer does not degrade within human life time is usually considered non-degradable. Today the market for polyolefin like LDPE, HDPE, PP microfilms used as packaging carry bags is quite large. Polyolefin in their unmodified form are resistant to destruction by biological agents. When these polymers are compounded with additives or plasticizers, the resultant polymer is affected by microorganism in various degrees. The percentage weight loss with pseudomonas aeruginosa, staphylococcus, aspergillus niger, penicillium and consortium was about 19%. The percentage weight loss with escheritia coli ranges from 8-33%.

FACTORS AFFECTING BIODEGRADABILITY:

Synthetic polymers are inherently resistant to biological attack. But susceptibility to biodegradation varies and is affected by:

1. Plasticizers
2. Additives
3. Water uptake
4. Crystallinity and molecular weight
5. The type of chemical bond
6. Copolymer composition
7. pH

8. Enzymatic degradation

POLYMER MODIFICATION

Polymers are modified so an environmentally acceptable polymer can be developed.

The modification include blends with other natural and synthetic polymers, grafting of another polymeric composition and chemical modification to introduce desirable functional group by oxidation or some other simple chemical reaction such as esterification or etherification.

THEORY OF PLASTICIZING

Plasticizers are occasionally used as processing aids in highly cross linked polymers. Plasticizers appear to function in polar, mainly by masking polar sites in the chain and there by reducing hydrogen bonding. In all polymers, plasticizer tends to force the chain apart, giving them greater freedom of movement and also reducing van Der Waals forces between the chains.

Based on the theory that:

1. There are no plasticizers that are completely free from fungal or bacterial attacks.
2. Susceptibility of microbial attack increases as the plasticizer level increases.

EXPERIMENTAL

LDPE film grade was compounded with Butyl stearate, Cottonseed oil, Dioctyl phthalate, Epoxidized soyabeen oil, Linseed oil, Soyabeen oil, Groundnut oil and General purpose polyester plasticizers. The amount of plasticizers was varied from 5-25% (w/w). In this way 80 samples were prepared. The specimens were then subjected to the microorganisms that are most susceptible to the degradation. The microorganisms selected were pseudomonas aeruginosa, staphylococcus, escheritia coli, aspergillus niger, penicillium and consortium.

The specimens were subjected to Screening of biodegradation of specimen under agitation for assessing the biodegradability. Visual observation for cracks, holes, and breakdown of specimen are carried out periodically. Physical test for weight loss are carried out periodically.

SCREENING OF BIODEGRADATION OF SPECIMEN UNDER AGITATION:

- Specimens are weighed and subjected to the microorganisms and placed in open air under stagnant condition for one month.
- The specimens from Screening of biodegradation of specimen in open air are taken as the base specimen.
- Six chains of 80 samples each was prepared by inserting a sample and a plastic bead alternatively in a nylon monofilament.
- Six chains of 80 samples are placed in six different conical flasks and supernatant from Screening of biodegradation of specimen in open air test are added to it.
- The conical flasks are placed for continuous stirring.
- After 8 weeks the specimens are washed and allowed to dry for one day and weighed.

- Weight loss and percentage weight loss was calculated.
- The specimen was visually observed for physical changes on the surface like holes, cracks, surface finish etc.

RESULTS AND DISCUSSION

TABLE - I SPECIMEN WITH PSEUDOMONAS AERUGINOSA

INITIAL WEIGHT IN mg.	WEIGHT AFTER ONE MONTH IN mg.	WEIGHT LOSS IN mg.	% WEIGHT LOSS	WEIGHT AFTER 8WEEK IN mg.	WEIGHT LOSS IN mg.	% WEIGHT LOSS
22482	21609	873	3.88	17549	4060	18.79

TABLE - I SPECIMEN WITH STAPHYLOCOCCUS:

INITIAL WEIGHT IN mg.	WEIGHT AFTER ONE MONTH IN mg.	WEIGHT LOSS IN mg.	% WEIGHT LOSS	WEIGHT AFTER 8WEEK IN mg.	WEIGHT LOSS IN mg.	% WEIGHT LOSS
21141	20168	973	4.40	16482	3686	18.28

TABLE - III SPECIMEN WITH ESCHERITIA COLI

SPECI.	INI. WEIGHT IN mg.	WT. AFTER ONE MONTH IN mg.	WT. LOSS IN mg.	% WT. LOSS	WT. AFTER 8WEEK IN mg.	WT. LOSS IN mg.	% WT. LOSS
Groundnut oil 25%	392	357	35	8.93	238	119	33.33
Soya been oil17.5%	182	176	6	3.3	144	32	18.18
Linseed oil 10%	268	239	29	10.82	206	33	13.18
Dioctyl phthalate 22.5%	309	292	17	5.5	255	37	12.67
Soya been oil 5%	135	130	5	3.7	114	16	12.31
G.P.Polyester 7.5%	306	292	14	4.58	267	25	8.56
Soya been oil 20%	226	211	15	6.64	193	18	8.53
Groundnut	223	207	16	7.17	190	17	8.21

oil 15%							
Soya been oil 22.5%	230	211	19	8.26	194	17	8.06
Soya been oil 2.5%	131	125	6	4.58	115	10	8.0

TABLE - IV SPECIMEN WITH ASPERGILLUS NIGER

INITIAL WEIGHT IN mg.	WEIGHT AFTER ONE MONTH IN mg.	WEIGHT LOSS IN mg.	% WEIGHT LOSS	WEIGHT AFTER 8WEEK IN mg.	WEIGHT LOSS IN mg.	% WEIGHT LOSS
22175	21225	950	4.28	17395	3830	18.04

TABLE - V SPECIMEN WITH PENICILLIUM

INITIAL WEIGHT IN mg.	WEIGHT AFTER ONE MONTH IN mg.	WEIGHT LOSS IN mg.	% WEIGHT LOSS	WEIGHT AFTER 8WEEK IN mg.	WEIGHT LOSS IN mg.	% WEIGHT LOSS
21088	20040	1048	4.97	16424	3616	18.04

TABLE - VI SPECIMEN WITH CONSORTIUM

INITIAL WEIGHT IN mg.	WEIGHT AFTER ONE MONTH IN mg.	WEIGHT LOSS IN mg.	% WEIGHT LOSS	WEIGHT AFTER 8WEEK IN mg.	WEIGHT LOSS IN mg.	% WEIGHT LOSS
23657	22616	1041	4.4	18665	3951	17.47

1. Of six chains placed in six different conical flasks, only the chain in the supernatant containing E-Coli as the microorganism remained unbroken and the specimens from the other five chains inserted in the nylon monofilament were shattered from the chain due to the dissolution of the nylon monofilament. Hence the total weight of the samples and the total weight of the sample and the total weight loss is considered.
2. The adopted culture has improved biodegradability of the nylon monofilament.
3. Total weight loss is approximately between 17.47-18.79%
4. The % weight loss is faster when the specimen is placed under agitation.
5. The weight loss is between 3.88-15% with Screening of biodegradation of specimen in open air test.

CONCLUSIONS:

1. The basic principle of the experiment is when a plasticizer is included in the plastic composition; it improves the extensibility of the plastics melt by the way of sliding the polymer chains over each other. This sliding of chains in turn reduces the overall tensile strength of the plastic by the way of reducing the binding forces between the two adjacent chains.
2. When these binding forces between the chains are reduced, it will be easier for the microorganism to attack on the weakened, individual chains and get nutrition for the growth and thus the degradation can be continued.
3. The initial nutrition is obtained from the plasticizer which exudes from the plastics specimen.
4. The plasticizer when exudes out of the polymeric chains, leave space between the chains. This in turn increases the distance between the chains, thus further weakening the binding forces between the chains.

Other test methods for assessing biodegradability should also be employed, for example growth ratings ASTM G-21, Colony growth profile on specimen in broth (liquid) medium and Soil burial test. Individual microorganism can be separated and their biodegradability can be checked individually. New micro flora can be developed by growing adopted microorganism in the soil nutrition by the plastic specimen. This microorganism can further be developed individually and characterized by their ability and the rate of biodegradability of the plastic films. The film thickness, plasticizer concentration, commercial production and cost effectiveness can be optimized. Biodegradability of other plastic material like PP, HDPE, GPPS, LLDPE, HMHDPE etc., can be tested using the same plasticizers i.e. butyl stearate, soya been oil, linseed oil, ground nut oil etc.

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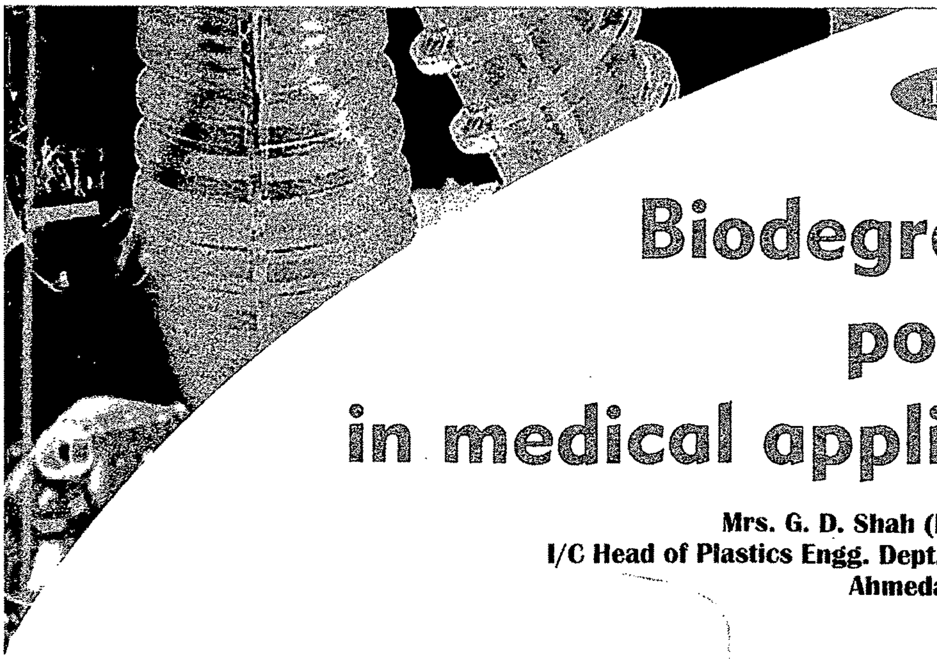

Biodegradable polymers in medical application

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BIODEGRADABLE polymers are widely used as biomaterials in medicine to replace a diseased part of the body to assist in healing to improve function, to correct cosmetic problems, to aid treatment and for diagnosis. There may be a variety of reasons, but the most basic begins with the physician's simple desire to have a device that can be used as an implant and will not require a second surgical intervention for removal. The general criteria for selecting a polymer for use as a biomaterial are to match the mechanical properties and the time of degradation to the needs of the application. The ideal polymer for a particular application would be configured so that:

It has mechanical properties that match the application, remaining sufficiently strong until the surrounding tissue has healed.

- It does not invoke an inflammatory or toxic response.
- It is metabolized in the body after fulfilling its purpose, leaving no trace.
- It is easily processable into the final product form.
- It demonstrates acceptable shelf life.
- It is easily sterilized.

Biomedical polymers in medicine and surgery are currently widely used, and include intra-corporeal, Para-corporeal or extra-corporeal applications.

Intracorporeal (Implanted) material

1. Temporary device
2. Surgical dressings
3. Sutures
4. Adhesives
5. Polymeric inter medullar nails
6. Polymer fiber composite bone plasters
7. Sciple semi permanent devices
8. Tendons
9. Reinforcing meshes
10. Heart valves
11. Joint reconstruction and bone cement
12. Tubular devices
13. Vascular grafts
14. Hydrocephalic drains
15. Esophageal prosthesis
16. Uretor segments
17. Gastro intestinal segments
18. Soft tissue replacement material for cosmetic reconstruction
19. Intraocular and contact lenses
20. Drug delivery implants
21. Artificial kidney/blood dialysis
22. Artificial lung/blood oxygenation
23. Artificial heart
24. Artificial pancreas/insulin delivery system

Para-corporeal or extra-corporeal material

1. Catheters
2. Blood bags
3. Pharmaceutical containers
4. Tubing
5. Syringes
6. Surgical instruments
7. Sterile and non sterile packaging material
8. Disposable in health care delivery

Biodegradable polymers for specialised application

1. Knitted bags from γ-irradiated PP fibers for biodegradable containers for machines planting of trees.
2. Block copolymers of low molecular weight, aliphatic polyesters of low molecular weight, aliphatic polyamide for biodegradable mulch film used as a thermal insulator in agriculture.
3. Small thin white wafers about the size of a dime, of biodegradable polymer containing chemotherapeutic agents

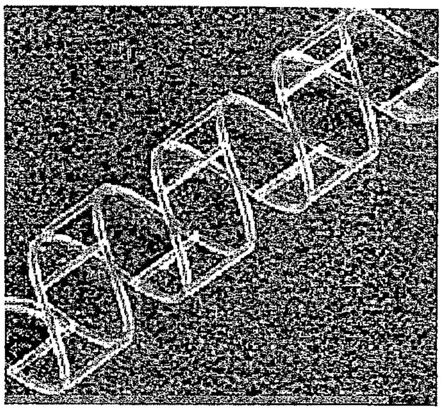
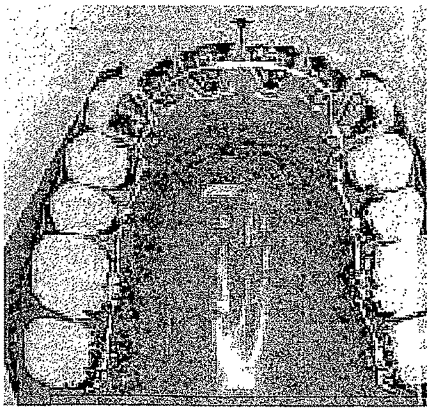


Fig. A biodegradable intravascular stent prototype is molded from a blend of polylactide and trimethylene carbonate

are used for brain tumors. Here the dime is placed directly on the brain after the tumor is taken out. Over the next three weeks or so, the little container dissolves allowing the drugs to work directly on the brain.

4. Gelatin is widely used as biological glue in surgical operations, in various industrial applications such as food products (stabilizers, thickeners, texturisers, meat packaging and other food processing), pharmaceutical technology (hard and soft gelatin capsules and gelatin coated tablets) and photographic films.
5. Lactide and glycolide polyesters and more recently the poly caprolactone system are used for delivery of tetracycline for periodontal disease and various vaccines.
6. Ester type system involving poly anhydrides are specially designed for delivery of anticancer drugs in the carcinal compartment.
7. Poly phosphazene polymers show interesting delivery profile for steroids and anesthetics.
8. Starch based thermoplastic composites, corn starch blended with ethylene vinyl alcohol or on corn starch blended with cellulose acetate when reinforced with hydroxyl lapatite is used as bone bonding and orthopedic temporary bone replacement/fixation.
9. Hydro gels of poly hydroxyl ethyl /L-glutamine and poly hydroxyl propyl L-glutamine are used as implantable drug release system.
10. Antimicrobial or antibiotic agent combined with a solution of poly glycolic acid or copolymer of lactic or poly glycolic acid is used for treating ophthalmological conditions like glaucoma or dry eye syndrome.
11. Poly glycolic acids and poly lactic acids are used as sutures, interface screws, pins, anchors for sutures, cement restrictor.
12. P dioxanone copolymers are used as monofilament sutures, legating clips, orthopedic pins, meshes, bone waxes, coatings for sutures, soft tissue augmentation and drug delivery vehicle.
13. Poly capralactone has main application as drug delivery vehicle, sutures. The copolymer of PCL with other co monomers like glycolide, lactide, and 1, 5-dioepan-2, 1 and blends of PCL with other polymers like poly hydroxy calerate and poly hydroxyl butyrate are used as suture coatings, absorbable medical device, micro porous intravascular stents as a support to auto logous vein grafts, nerve guide device, external casting material for broken bones, custom dental impression trays to fabricate a radiation therapy mask.
14. Poly hydroxy alkanoates as biodegradable films in various environments such as soil sludge and sea water, lake water, enzymatic degradable films.
15. Poly propylene fumarate as biodegradable injectable bone cement, drug delivery agent to deliver bio active molecules to the bone, carrier for cells, genes and bio active molecules to induce wound repair and facilitate tissue formation and re modeling.
16. Poly ortho esters used as drug release vehicle treatment of burns, re-ossification of experimental bone defects.
17. Poly phosphate esters used as synthetic material for bone repair, dental restoration, and fracture fixation.
18. Poly ester amides used in drug delivery system and tissue engineering.
19. Poly anhydrides used for controlled drug delivery system, implant for the treatment of brain tumors treating chronic bone infections.
20. Poly phosphazenes used as bio materials for cardio vascular and dental uses, controlled drug delivery system, tissue replacement, coating materials for artificial implants bio resorbable tubular nerve guides prosthesis, denture liner.
21. Poly alkyl cyano acrylates used as drug particulate carriers, therapeutic treatment of cancers, intra cellular infections and ophthalmic diseases.
22. Hydro gels used for control of post operative wounds healing, prevent post operative adhesion, controlled release gastric retention device, targeted for long term oral drug delivery immobilization of enzymes, incorporate nerve growth factor to control the nervous tissue regeneration, as skin substitutes, absorbent haemostatic dressing for



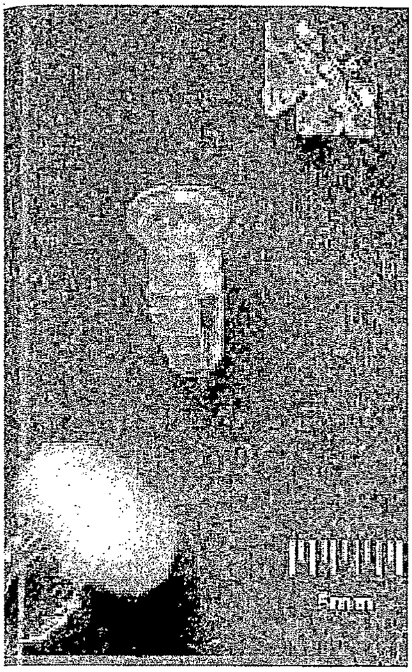
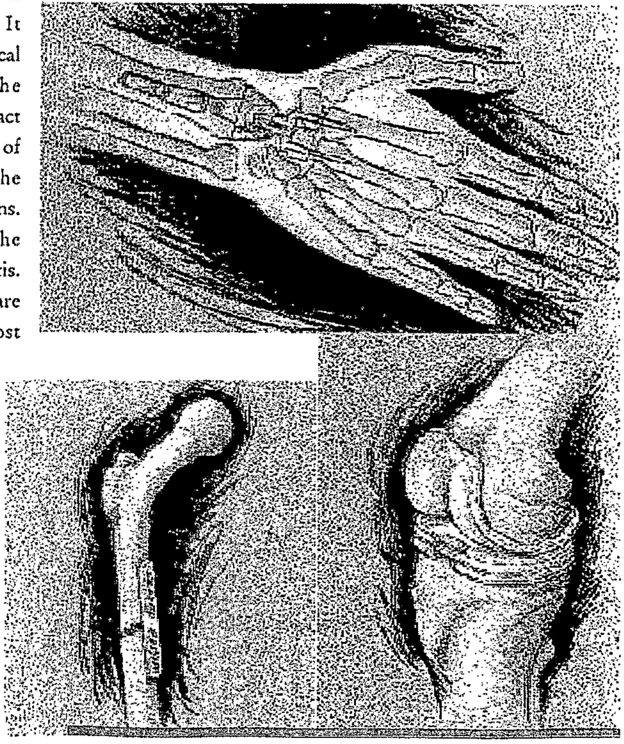


Fig A cartilage repair unit injection molded from biodegradable polylactide (PLA).

skin wounds, food industry, intelligent bio sensor for $Ca^{2}+$ binding agent in conventional wet granulation process water absorbents, hydro gel when adhered to the tissue - prevents adhesion between organs.

23. Poly oxamers use for treatment of tissue ischemia and reperfusion injury, reduction of blood viscosity, interactions with fibrin result ion reduced the time of clot formation, reduction of hemolysis during cardio pulmonary by pass, reduction of leakage of fluorescent calcium from thermally and electrically damage cells, prevention of post surgical adhesions as peritoneal adhesion, spinal adhesion, and drug delivery.
24. Tyrosine derived polymers use in orthopedic implants, small bone fixation devices like pins, screw, plates, and coatings for blood contacting devices and drug delivery systems.
25. Alginates used in pharmaceutical preparation, cell entrapment, enzyme immobilization.
26. Arabino galactan used in industries such as printing, mining, carbon black, food etc. used in cell separation, cosmetic formulation, pharmaceutical dosage form, FDA approved food ingredient.
27. Chitin and Chitosan promote the healing of wounds, some bio activating effects. Braided fibers, sheets porous sponges made from chitin and chitosan are applied clinically in the form of absorbable sutures threads and temporary dressing for the skin and soft tissues defects. Drug delivery matrices as filling for bone defects, as internal fixation devices for bone fracture. Artificial skin made from chitin is available in the form of non woven fabric.
28. Dextran is used for controlled delivery of bio active proteins.
29. Hyaluronic acid used as powder, film or a coating on various substrates. Primarily used in cataract surgery. It minimizes the surgical trauma during the removal of the cataract lens and introduction of its replacement, the intraocular plastic lens. Preparation for the treatment of arthritis. Other applications are management of post surgical adhesion in abdominal, cardiac, musculoskeletal and neurological procedures.
30. Starch used in food and paper industry, textile manufacturers, pharmacology, controlled drug delivery system modifying natural and synthetic polymers to meet the growing needs.
31. Oxidized cellulose as topical absorbable haemostatic agent is used in various surgical procedures like neuro, orthopedic, genecology, onorectal, abdominal, cardio vascular, thoracic, head, neck, pelvic and skin and subcutaneous time surgery. The knitted fabric form prevents the post operative pelvic adhesions.
32. Collagen in form of coating fibers films membranes, solutions, matrices, sponges, suspension tapes, tubes and sealants used for closing surgical wounds and incisions, for hernia repairs, tubes for replacement of esophagus, peripheral nerve, nerve regeneration, repair of the tympanic membrane, for cartilage meniscus and bone repair of liver injury, proactive barrier during brain surgery, wound repair collagen solutions are used as injectable augmentation system for arterial immobilization, cutenous defects,



fracture healing, spinal chord regeneration, correction of urinary in continence, tendon gliding function restoration and lung gluing collagen substrates are used for growth of skin cells.

33. Fibrinogen and fibrin sheets or foam are used to assist hemostats, film for replacement of the dura meter over the brain in head injuries plasma derivative for treatment of hemophilia. Fibrin glue is used in nerve repair, in neurosurgery and ophthalmic surgery, sealing of dura meter prevent cerebrospinal fluid leakage, sealing of lens perforation, corneal ulcer repair, arresting bleeding of liver or spleen or external bleeding in patients with hemophilia, skin grafting craniofacial reconstruction.
34. Protein based polymers are used in drug delivery and tissue reconstruction.

Processing

All commercially available biodegradable polymers can be melt processed by conventional means such as injection molding, compression molding, and extrusion. As with packaging, special consideration needs to be given to the exclusion of moisture from the material before melt processing to prevent hydrolytic degradation. Special care must be taken to dry the polymers before processing and to rigorously exclude humidity during processing. Because most biodegradable polymers have been synthesized by ring-opening polymerization, a thermodynamic equilibrium exists between the forward or polymerization reaction and the reverse reaction that results in monomer formation. Excessively high processing temperatures may result in monomer formation during the molding or extrusion process. The presence of excess monomer can act as a plasticizer, changing the material's mechanical properties, and can catalyze the hydrolysis of the device, thus altering degradation kinetics. Therefore, these materials should be processed at the lowest temperatures possible.

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