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Education in Chemical Science and Technology

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Education in Chemical Science and Technology

VOLUME 3 **AUGUST 2015**

PREFACE

Keeping in mind the specific need of students of schools, colleges, and universities, the Indian Chemical Society has undertaken the arduous task to bring out a biannual periodical "Education in Chemical Science and Technology" with a hope that the periodical would fulfill the requirement of advance undergraduate and postgraduate students having diverse background and training. The first issue, published in August 02, 2013 has been widely appreciated and we hope that this third issue of the periodical would be equally appreciated by the budding researchers in basic chemistry, chemical technology, and interdisciplinary subjects.

I express our gratitude to Professor Mahesh C. Chattopadhyaya, former President, Indian Chemical Society and Professor R. N. Prasad, President, Indian Chemical Society for their initiative for the publication of this periodical. I sincerely acknowledge with admiration the scholastic contributions of the authors who kindly responded very quickly for contributing their articles.

I also express my thanks to Dr. Rahul Bhattacharya, Executive Officer, Sri Mahananda Khamrui, and all the employees of the Indian Chemical Society and M/s. Auto-Print and Publicity House for their hard work and commitment.

In spite of our best efforts some inadvertent errors might have crept in, for which I tender my sincere apology.

I sincerely believe that the present issue would be warmly received by those for whom it is intended. We shall highly appreciate receiving any suggestion and criticism from the users of this periodical.

D. C. Mukherjee
Honorary Secretary
Indian Chemical Society

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Education in Chemical Science and Technology

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PREFACE

It is our great pleasure that the 2nd edition of the 3rd issue of the biannual priodical "Education in Chemical Science and Technology" is being published in the re-edited form on August 2022, to celebrate the auspicious 161st Birth Anniversary of Acharya Prafulla Chandra Ray, the "Father of Indian Chemistry". It is to mention that the 1st edition of this issue was initially brought out in August 2015, as the previous issues were extremely popular among students and teachers. Prof. D. C. Mukherjee, the then Hon. Secretary of the Indian Chemical Society (ICS), took the responsibility to edit the issue and seven beautiful articles were considered to be printed. It includes – 'Time economic innovative pedagogies in chemical science' by Das *et al.*; 'Magnetic nanoparticles and their applications' by Gautam *et al.*; 'Homoaromaticity' by Basu *et al.*; 'Pams Quantum Periodic Table' by D. N. Raju, 'Extraction of copper from small electronic devices' by A. Kumari *et al.*; 'Trace analysis of uranium in coal fly ash by fluorimetry' by Sarangi *et al*. and 'Zinc sensor' by Bhanja *et al*. The issue was highly recognized among the readers.

Keeping in mind the growing popularity and specific needs of the students and teachers, the present Council of the ICS has decided to publish the 2nd edition of the 3rd issue with International Standard Book Number (ISBN). It is now an outcome of the original issue with four additional articles as newly appended along with earlier seven articles in its content.

The newly entrant four articles are contributed from Prof. Avijit Banerji, former Professor, Department of Chemistry, University of Calcutta and presently at Central Ayurveda Research Institute, Kolkata, Prof. Niranjan Karak of Tezpur University, Assam, Prof. Samaresh Bhattacharya of Jadavpur University, Kolkata and Dr. Sibaprasad Maity of Haldia Institute of Technology, Haldia, West Bengal, as the corresponding authors in their respective articles. Overall, the four new articles shade lights on both hardcore

and applied chemical fields, covering the topics 'Ruthenium(IV)-oxo species and their utilization in oxidation reactions', '[3+2] cycloaddition reactions from the molecular electron density perspective', and 'Bioplastics: greener alternatives to conventional plastics, its opportunities and challenges'. All articles in this re-edited issue are peer reviewed as per publication protocol and seem to arouse academic interests in the chemistry fraternity; especially the undergraduate and postgraduate student sections to supplement their curriculum activities and also the research scholars to pursue their exploration.

The Indian Chemical Society gratefully acknowledges all the authors for their scholastic contribution. The Council members and advisors of the ICS deserve special thanks for their constant support in publishing this re-edited issue. We sincerely thank to the cover page designer of the 1st edition, which is used 'as-it-is' in this issue. Due thanks are extended to the Office Staff of the Society as well as the Press for their cooperation.

In spite of our best efforts some unintended errors might have squirmed, for which we tender our earnest apology. We sincerely believe that the present issue would be warmly received by all possible readers for whom it is purposive. We shall highly appreciate receiving all possible criticism and positive suggestions from the readers.

Prof. G. D. Yadav
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C O N T E N T S

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AUTHOR INDEX

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Bioplastics: A Greener Alternatives to conventional plastics

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Aim: The biodegradable polymers appear as an alternative to conventional plastic materials which are mostly non-biodegradable in nature and creating a long term environment concern. But we can't deny the use of polymers in the present scenario. The growing social concerns and environmental awareness have triggered the search for new polymeric materials and processes that are well-suited with the environment. People have been keenly attracted to the concept and perceived environmental advantages to biodegradable plastics. The polymers, if biodegradable, can be disposed of in the ecologically sound manner, through waste management. Considering the necessity, in addition to improving the degradation pattern of these synthetic poly-

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meric materials, the development of new polymeric materials which might be degraded under environmental conditions draws our attention.

Keywords: Sustainabillity, bioplastics, biodegradation.

1. Introduction

Polymers are one of the most important materials which have garnered a universal presence in our daily lives with remarkable versatility in form and function. Polymers are macromolecules of higher molecular mass consisting of a long chain backbone of smaller repeating units, built up by linking of a large number of small molecules, named as monomers. In earlier days we were dependent on cotton, jute and some agricultural products for clothing, and wood, metal, glass, stone and bricks etc. for manufacture of the materials needed for a civilized life. But now the synthetic fibres have brought a revolution in the textile industry. Presently terylene and nylons have almost replaced cotton and silk. It is very difficult to think of a day without synthetic or natural polymers because of the fast growing demand of new materials used in buildings, automobiles, aircraft frame, irrigation, daily utensils, electronic gadgets etc. - for better human living and comfort. Inertness of the plastics under environmental conditions make it useful as food packaging material and for storing of other substances, but unfortunately due to the same reason, on disposal they last for centuries in landfill sites, creating difficulties to find more spaces for landfill sites and also it leaches toxins slowly into the soil as time passes. The microorganism may not degrade those plastics most of the time properly into biomasses; if we go for incineration it emits large quantities of CO_2 which may cause global warming. Recycling plastics becomes also difficult and expensive. Thus scientists are thinking about biodegradable plastic which might be an alternative to conventional plastic, to be prepared easily and

economically and can be disposed of in a safe and ecologically sound manner.

2. Concern with plastics

Degradable plastics may be photodegradable or Oxo-degradable which disintegrate into small pieces when exposed to sunlight and oxygen, semi-biodegradable or 100% bio-degradable which ensure degradation of plastics by bacteria, fungi and algae etc. into biomass ultimately. Sustainability requires the natural processes of degradation of these plastics, such that the basic building blocks can be decomposed by nature to make a new life form. Petrochemicals based plastics are not designed by nature and obviously not degraded by natural processes. Plastics are the polymerized material which is easy to mould into a variety of products of different shape and size. It is easy to spot them around us at every corner and become an integral part of our lives due to their versatile nature like light weight, possess thermal and electrical insulation and long lasting. The mostly used polymers like PE, PP, PVC, PS and PET, are produced by chemical synthesis using petroleum feedstock. Packaging without plastics is just what we can't imagine in present days due to its low cost, light weight and durability. When the designing of synthetic polymers for packaging comes to our mind, good barrier character to water vapour, oxygen and mechanical performance as well as durability are the prime matters come to our mind but hardly about their degradability and recyclability. The polyethylene terephthalate (PET), polyethylene and poly-propylene are the most widely used polymeric materials but till date we are worried about their degradability and/or effective recyclability[1]. As reported in Science article (Science 304, 838, 2004) the plastic debris around the globe can be decomposed into microscopic granules or fibre like fragments, which have been storing steadily in the oceans and marine animals, seabird species are known to have ingested fine synthetic polymer fragments that have been mistakenly

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consumed as their food, as seen sometimes in their digestive tract. The unfortunate death of shore birds which play a vital role in the ecosystem to maintain population sizes of fishes and crustaceans might be a matter of great concern.

3. Bio-plastics and degradation

These plastics are no doubt durable but their lack of biodegradability is now our primary concern. But overuse of single use plastics has led to a global, environmental catastrophe. Lack of recyclability or degradability into building blocks and/or biomass is not only creating plastics waste but also a great loss to the economy. Several efforts have been made to address such problems during the last couple of years, such as development of effective catalysts for effective depolymerisation of plastics into building blocks and/or monomers to reprocess these, designing of additives for chemical recycling, copolymer like PT6HP-co-P_YBL, of better barrier and mechanical properties comparable to petroleum-based polymers are noteworthy[2–11].

Due to concern over climate change, limitation on supply of fossil carbon source, there is increasing interest in bioplastics. Polymers with biological relevance can be classified as:

(i) Biopolymers - i.e. polymers from plants, animals and microorganisms. eg. starch, cellulose, proteins,

(ii) Biobased polymers - which are derived from renewable natural resources like plants, animals or microorganisms, as opposed to petroleum based resources. e.g. BioPE, BioPET

(iii) Biodegradable polymers - They might be biopolymers, biobased polymers and even polymers from petroleum based resources. e.g. Polyvinyl alcohol

The words ‘bioplastic’ and ‘biodegradable plastic’ are similar but not synonymous. Biodegradable plastics are commonly produced from renewable raw materials, micro-organisms, petrochemicals or combination of all of these. They are usually

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decomposed by the action of living organisms, into water, carbon dioxide and/or biomass. Biodegradable plastics are commonly used for disposable items like crockery-dishes, cups, glasses; cutlery-spoons; packaging-bags, bottles; and different food service containers. In principle they could replace conventional plastics, however their cost and performance are a matter of worry. In a few countries use of biodegradable plastic bags and shoppers have been compulsory by law.

Biodegradable generally refers to a substance that can be broken down by microorganisms in the environment within a stipulated period of time. Effective biodegradation requires specific environmental conditions like temperature and level of aeration, allowing microorganisms to convert the materials into other natural substances such as water, carbon dioxide and compost. Biodegradability is directly related to the chemical structure of the materials, not to the origin of raw materials. Biodegradation is a function of humidity, temperature, pH, level of oxygen, concentration of salts and various nutrients. Presence of fungicides may also affect biodegradability. Structure and properties of polymers like molar mass, chemical reactivity, cross-linking, porosity, mechanical strength play important roles towards their biodegradability. e.g. polymers of very high molecular mass are less susceptible to biodegradation.

Thus biodegradable polymers draw immense attention from sensible communities. People are searching for biodegradable plastics which will exhibit better resistance to penetration of water vapour, oxygen and carbon dioxide as well as considerable elongation at break and also be economically viable. There are different polymers of biological relevance. Biopolymers like proteins, polysaccharides which are generated from plants, animals and microorganisms itself. Biobased polymers like BioPE, BioPET which are prepared through polymerization of some raw materials coming from some natural resources or renewable sources rather than petroleum resources. But biodedegradable polymers may include bio-

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polymers, biobased polymers and also polymers from petroleum based resources but not all are biodegradable. During biodegradation of polymers it seems the macromolecules are converted into CO_2 under aerobic condition and CH_4 under anaerobic condition along with some other residues and biomasses. These polymers may be photodegradable, oxo-degradable or even compostable, operated by microorganisms, small insects and/or earthworms to produce humus. Degradation of polyhydroxybutyrate is mainly based on depolymerisation by hydrolase enzymes into oligomers, dimers or monomers and finally into CO_2 or CH_4 and other residues depending on availability of oxygen.

Plastics are referred to as 'green' if they resemble either or all of the properties like-biodegradability or compostability after end of life, source renewability, environmentally friendly processing. 'Green plastics' are recognized as a possible solution for concerns regarding the use of traditional petroleum based plastics.

Compostable plastic is one that meets the scientifically recognised standards of compostability regardless of the origin of carbon. European Norm is **EN 13432**, and USA Norm is **ASTM D6400**

As for example as per **ASTM D6400-** the main factors that the plastics materials should exhibit, to be considered as compostable are-

1. Mineralization:

- 90% conversion to carbon dioxide, water and biomass through the action of microorganisms.
- The same rate of degradation as other organic waste
- Time period of degradation 180 days or less

2. Fragmentation:

Not more than 10% of the original dry weight of test material shall fail to pass through a 2 mm fraction sieve.

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3. The impact on the environment:

No negative impact on flora and fauna

Biodegradability of polymers involves (a) copolymerization of monomers which are vulnerable to micro-organisms and (b) blending of biodegradable additive/polymer with non-biodegradable polymer. Polymers can be degraded by (a) high energy radiation (b) heat and oxygen (c) microbes.

Photo degradation initiated by the absorption of light energy by certain groups present in the polymer molecule. It results in the scission of the long chain macromolecule into smaller fragments. Photo degradation of polymers requires either the presence of a photo responsive group within the polymers chain itself or some additive. *Thermal degradation* normally receives support from oxygen in air and so it is also known as thermo oxidative degradation. Rupturing of macromolecules generally results in radical sites which react with oxygen to form peroxy radicals thus converting the macromolecules into smaller fragments.

Photo-biodegradable plastics are the synthetic polymers which are incorporated with photo sensitizer, like diketones, ferrocene derivatives and carbonyl containing species, or co-polymers for purpose of weakening the bond of the polymer in presence of ultraviolet radiation. Photodegradation may be useful in applications where littering is an issue and pose a threat to animal and marine life.

Plastic Additives- Prodegradant Concentrates (PDCs) promote oxidation processes that break the plastic down into brittle, low molecular weight fragments. Microorganisms gobble up the fragments as they disintegrate, turning them into CO_2, water, non harmful residue and/or biomasses. As noted, PDCs being present in 3% with PE can promote nearly 95% degradation into bacteria friendly fragments within 4 weeks. They are not biodegradable rather bioerodible. They are used to manufacture

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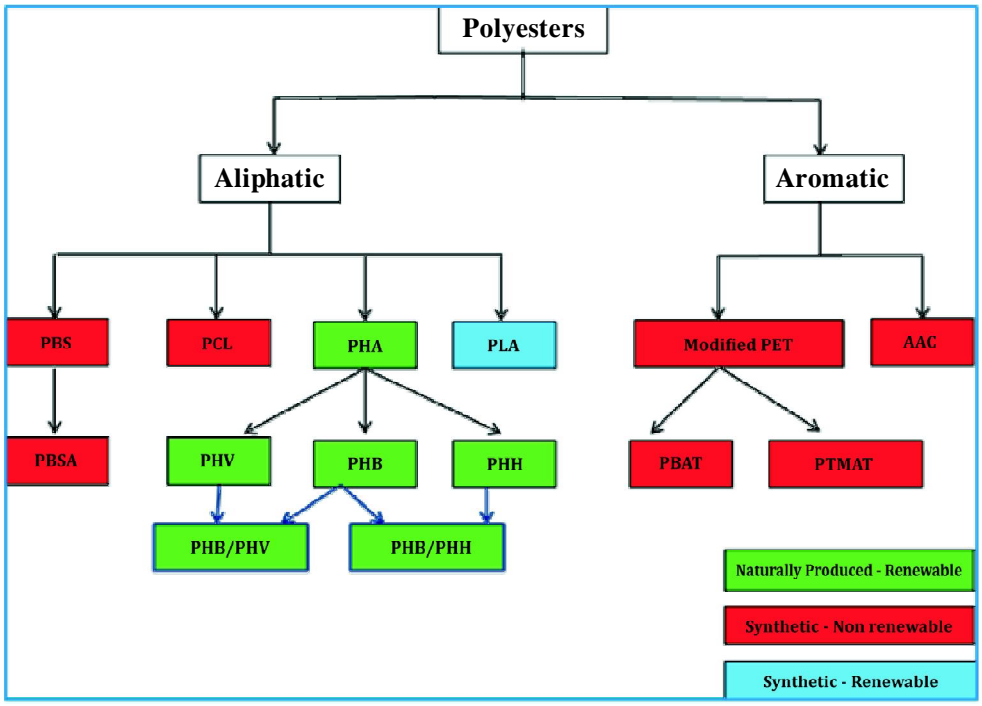
single use plastics such as disposable diapers, thin shopping bags, food containers, landfill covers etc.

4. Biobased plastics

Few plastics* which are enlisted below, among these few are naturally produced and renewable (Green boxes), few are synthetic and non-renewable (red boxes) but very few are synthetic and renewable (sky colour box).



*PBS: Polybutylene succinate, PCL: Polycaprolactone, PHA: Polyhydroxyalkanoates, PLA: Polylactic acid, PBSA: Polybutylene Succinate adipate, PHV: Polyhydroxyvalerate, PHB: Polyhydroxybutyrate, PHH: Polyhydroxyhexanoate, PET: Polyethylene Terephthalate, AAC: Aliphatic Aromatic copolyesters, PBAT: Polybutyleneadipate terephthalate, PTMAT: Polymethylene Adipate Terephthalate

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*Type of plastic	Applications	Degradation
PHA	Blow and injection moulded bottles and plastic films	10 weeks in compost
PLA	Drink cups, take away food trays, containers and planter boxes.	2 weeks via hydrolysis
PHBH	Mono/multilayer films	Under aerobic and anaerobic conditions
PCL	Film bags, food contact foam trays.	6 weeks in compost
PBS	Mulch film, packaging films, and flushable hygiene products.	8 weeks in garden soil
AAC	Commercial food wrap for fruit and vegetables.	12 weeks via composting

Agricultural waste and Food waste are the most common environmental waste we see in our daily life. Production of bioplastics from those wastes which are easily available may be a renewable sustainable process. Biobased polymers derived from biomass which can be used as polymeric materials and/or with some chemical modifications or blending, like cellulose, cellulose acetate which is prepared by acetylation of plant cellulose, starches, chitin, modified starch etc. are used directly without any purification. There are also bio-engineered polymers which are biosynthesized by using microorganisms, it facilitates to achieve desired physical properties than chemically designed one of limited flexibility e.g. polyhydroxyalkanoates, polyglutamic acid etc. There are monomers of another class of polymer like PLA, PBS, bio-PET, that are derived from natural sources through biological and/or chemical processes to reduce the carbon footprint. Around 2010 analogous to petroleum based, engineering-grade biobased polymers like bio-PET, polyamide began to be of industrial interest[12–14]. PLA, polytrimethylene terephthalate(PTT), polyisosorbidecarbonate, polyethylene 2,5-furandicarboxylate(PEF) are noteworthy industrialized biobased polymers. PEF exhibits better gas barrier properties and so is used for bottles and other packaging materials in the food and beverage industry. Let us discuss some biodegradable/compostable polymers that are currently being used and their properties, as well as their synthesis.

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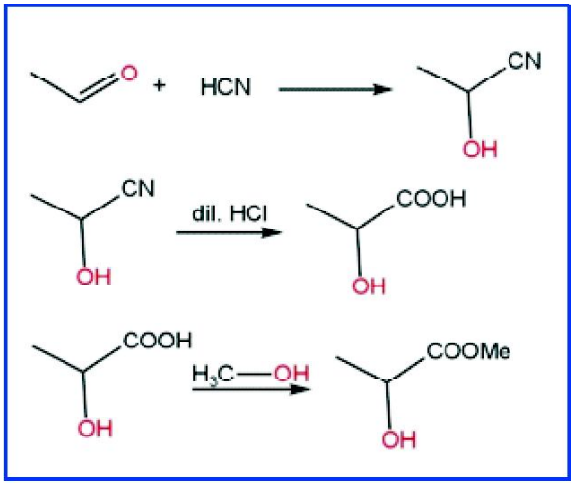
Aliphatic polyesters are the biodegradable polymers which are mostly studied. Low molecular weight polymers are prepared using difunctional monomers preferentially but ring opening polymerization is preferred to yield polymers of high molecular weight[15]. Aliphatic polyesters are classified as *polyhydroxyalkanoates* -polylactic acid, polyglycolic acid(PGA) and poly*alkene* dicarboxylates- polybutylene succinate, polyethylene succinate.

(i) Polylactic acid (PLA):

It is aliphatic polyester, prepared from D- and/or L- lactic acid or from ring opening polymerization of lactide - cyclic dimer of lactic acid. Renewable sources like fermented plant starch - corn, cassava, sugarcane etc are the notable raw materials. Lactic acid, the simplest 2-hydroxycarboxylic acid with a chiral carbon atom, is optically active. There are two optical isomers – L-lactic acid and D-lactic acid. Lactic acid can be extracted from fermentation of milk and laso sugars. Starch, glucose, lactose and maltose produced from corn and potatoes are used for lactic acid fermentation. The most employed worldwide process to get one given isomer of lactic acid is bacterial fermentation which leads to higher yield based on the type of bacteria chosen. Fermentation needs 3–5 days under pH 5 at about 40°C in presence of low concentration of oxygen.

Chemical synthesis of lactic acid can be performed in different ways but the most popular route is the following one.



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Acetaldehyde on reaction with HCN (as a source of which mixture of NaCN and HCl can be used) produces lactonitrile which on hydrolysis as lower pH using dilute HCl gives lactic acid, it is then converted into methyl lactate through esterification with methanol. This esterification facilitates recovery of lactic acid as methyl ester through distillation. Methyl lactate thus collected is hydrolysed back into lactic acid and methanol which is recycled back into the esterification process. Lactic acid can also be prepared from propionic acid by chlorination in presence of red phosphorus using Hell Volhardt Zelinsky reaction followed by hydrolysis, then the product collected through esterification, distillation and hydrolysis. Purification of lactic acid is expensive and determines process profitability. Although the large-scale production of lactic acid can be achieved by chemical methods, the processes do not accord with the standards of green chemistry.

Using D- and L- lactic acid isomers three forms of polylactic acid are prepared – poly-L-lactic acid (PLLA), poly-D-lactic acid (PDLA) and poly-D, L-lactic acid (PDLLA). Direct condensation polymerization, azeotropic dehydration condensation and lactide ring opening polymerization are the three major synthetic techniques for synthesis of PLA[16a].

PLA is more hydrophobic than polyglycolic acid (PGA) due to presence of side $-CH_3$ group, the glass transition temperature of commercial PLA is 63.8°C, tensile strength is 32.22 MPa and the elongation at break is 30.7%[16b]. poly(L-lactide) PLLA, the semi-crystalline polymer of L-lactide, is hard, transparent, elongation at break of 85–105% and 45–70 MPa tensile strength with glass transition temperature 53°C whereas poly(DL-lactide) PDLLA is amorphous, glass transition temperature 55°C, but much lower tensile strength. Physical properties of PLA are improved with more content of L-isomer of lactic acid[17]. PLA, one of the most useful bioplastic, is compostable i.e. disintegrates within artificial composting conditions but not naturally biodegradable. Degree of crystallinity decides the rate of degradation. It can also be enhanced by grafting. Brittleness and poor thermal stability are the demerits of PLA. Different companies commercialize PLA with various ratios of D/L

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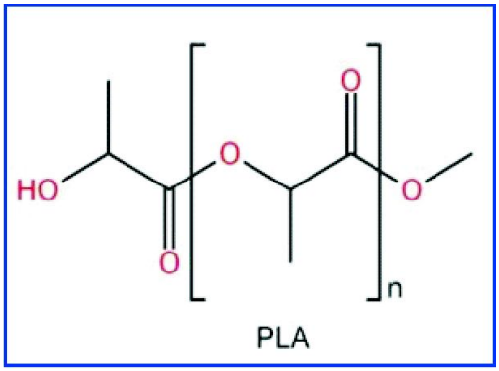
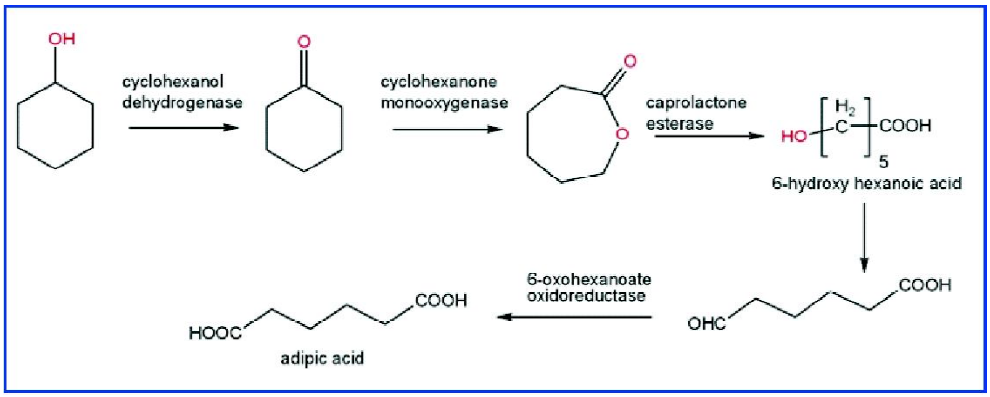
lactide[18]. Due to improved physical durability and processiblity it is being used in the packaging industry.



(ii) Polycaprolactone (PCL)

Polycaprolactone(PCL) due to its miscibility with a range of polymers, biodegradability and mechanical strength marks its importance. Mainly it can be prepared by the polycondensation of 6-hydroxyhexanoic acid and ring opening polymerization (ROP) of ε-caprolactone. Emphasis is given to the ROP pathway since it provides superior polymer quality[19a]. If we think on preparation of monomer, cyclohexanol can be oxidised by a number of microorganisms into adipic acid, during which both ε-caprolactone and 6-hydroxyhexanoic acid are intermediary products. Industrially, by oxidation of cyclohexanone with peracetic acid, ε-caprolactone can also be prepared.

Oxidation of Cyclohexanol to adipic acid:



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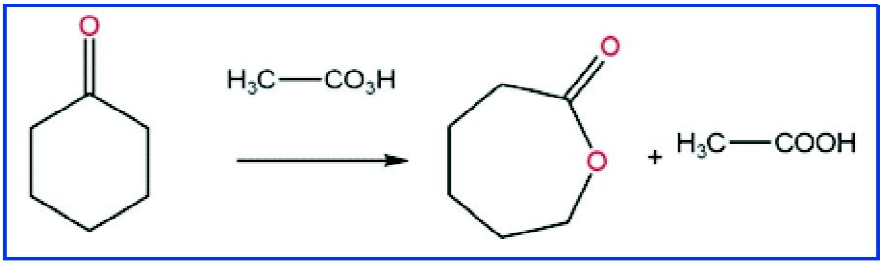
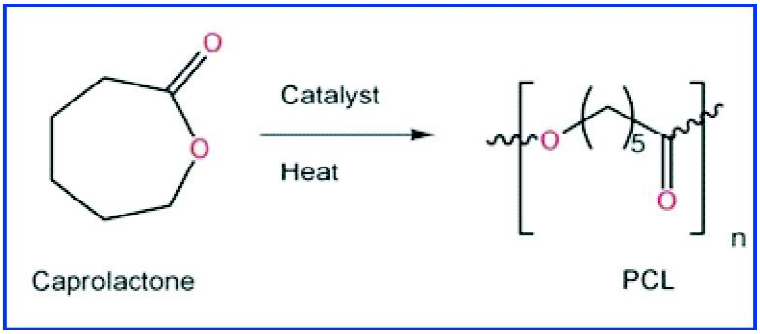
Production of ε-caprolactone from cyclohexanone:



Ring opening polymerization ε-caprolactone in presence of Tin(II) 2-ethylhexanoate catalyst yields PCL. It is a semi-rigid material at room temperature, with low tensile strength of 23 MPa and high elongation to break (~700%) and T_g is low nearly –60°C, and so PCL is often used as a soft block in polyurethane formulations. PCL is degradable in presence of enzymes and fungi[19b,c]. Copolymers of ε-caprolactone with lactide or glycolide have better degradation rate.



(iii) Polybutylene succinate (PBS) and polybutylene succinate-co-adipate (PBSA):

PBS is a thermoplastic resin of the polyester family. It is a biodegradable with properties that are comparable to poly-propylene. PBS is prepared by polycondensation of 1,4-butanediol and succinic acid.

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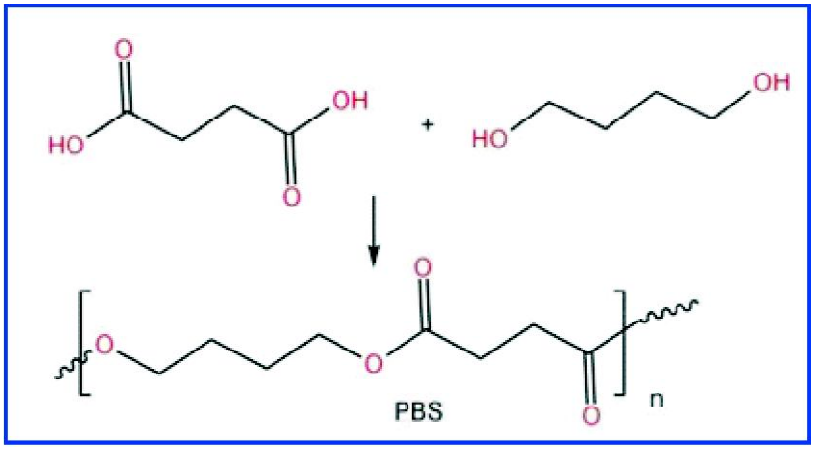
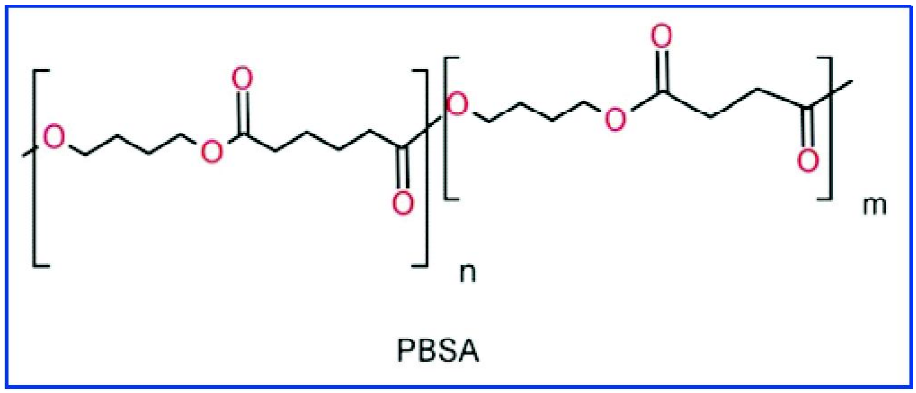


PBS is a white crystalline polymer, T_g is –45°C to –10°C, having melting point 90–120°C. Its elongation at break is nearly 330% and tensile strength 33 MPa. Poly(butylene succinate-co-butylene adipate) (PBSA) is prepared by co-condensation of 1,4-butanediol with succinic acid and adipic acid. All the monomers can be produced from renewable as well as petroleum based feedstock. Compared to PLA, PBSA is more flexible and does not require plasticizers. PBSA is useful in food packaging, mulch film, and hygiene products. PBSA degrades faster than PBS but they are known to biodegrade slower than PHAs. PBSA is less crystalline than PBS and is suited better to film applications.



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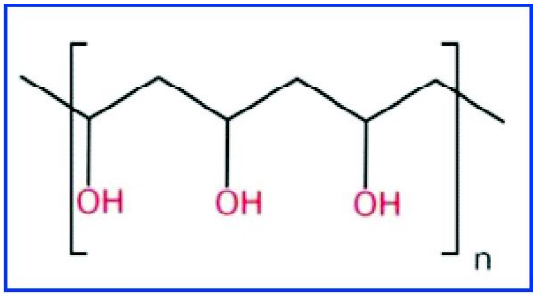
(iv) Starch based polymer/Starch blends:

Starch is a means of storing and obtaining energy in plants. Starch polymers by itself are brittle at room temperature, so plasticizers are required to blend during the process of starch gelatinization. Though all starches are biodegradable, not all plasticizers i.e. biodegradability of starch blend depends on the plasticizers used. Starch/PLA, starch/polycaprolactone, starch/ polybutylene-adipate-co-terephthalate are examples of biodegradable starch blends whereas starch/polyolefin blends are non biodegradable.

(v) Polyvinyl Alcohol (PVOH):

It is a well known synthetic colourless, odourless biodegradable polymer, used in a range of film applications from the lamination of safety glass to the packaging of laundry detergent. It is water soluble and can be degraded by activated sludge treatment.



(vi) Ethylene Vinyl Alcohol (EVOH):

It is flexible, crystal clear, glossy, water soluble synthetic copolymer, and is used as an oxygen barrier layer in multilayer film packaging, exhibits high resistance to hydrocarbons, oils and organic solvents. Its barrier resistance to oxygen, nitrogen and carbon dioxide makes it suitable for packaging food, drugs, cosmetics etc. Compared to other common films, EVOH has superior barrier properties but when exposed to moisture, it loses its barrier properties so very often it is used in a multi-layered film with materials such as PET, HDPE, PP etc. but its widespread use as biodegradable plastics is not so cost effective.

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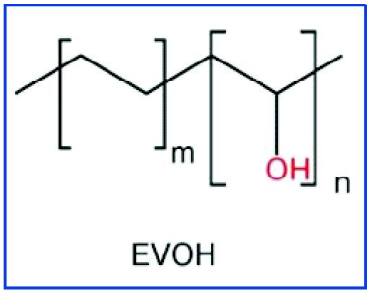
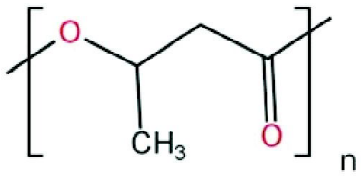


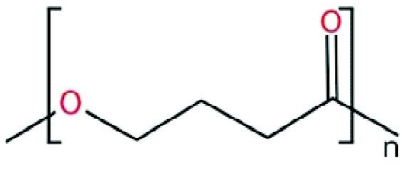
EVOH

(vii) Poly(hydroxyalkanoates) (PHAs):

They are the homopolymer or co-polymers of hydroxyalkanoates like poly(3-hydroxybutyrate) (P3HB) and poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (P(3HB-co-3HV)) respectively. PHAs from energy rich feed stock nowadays waste water on which bacteria (PHA producing bacteria) feed is extracted and processed into pallets or powder[20]. Though chemical synthesis of PHA via ring opening polymerization of lactones is possible but stereochemically uncontrolled, chain lengths in this case are shorter than biologically synthesized PHAs. In biological synthesis of P3HB, sugars are converted to acetates, with which coenzyme A complexes into acetylCoA. AcetylCoA is dimerized to acetoacetyl A and finally through reduction hydroxybutyryl CoA is polymerized. Glass transition temperature decreases as chain lengths of PHA increases. Melt temperature of P3HB is 160°C, while the melt temperature of P3HB-co-3HV is only 145°C. Compared to conventional petroleum-derived polymers processing PHAs is challenging because of their sensitivity to thermal degradation and slow solidification due to slow crystallization. The degradation temperature of PHAs is around 180°C.



Poly(3-hydoxybutyrate) P3HB



P4HB

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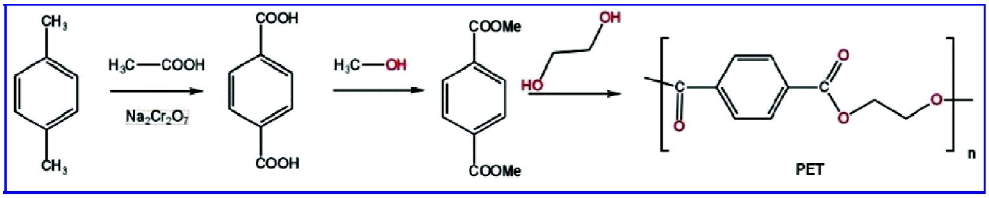
About 40% of overall polymeric materials used now-a-days is in the packaging sector, and among the polymers used in packaging applications PE, PP, PET and PS are most noteworthy. The Polyethylene terephthalate (PET) is a thermoplastic used in making bottles, films and also in the textile industry. It is composed of 70% terephthalic acid and 30% ethylene glycol by mass. In Bio-PET both monomers are the same but ethylene glycol is produced from renewable resources e.g. using ethanol from sugar cane. And it is in fact 20–40% more expensive than conventional PET. In the long term, production of completely biobased PET is yet to be achieved. Still there are some biobased polymers analogous to conventional plastics derived from petroleum.

Biobased Polyethylene (Bio-PE):

When ethylene, prepared from ethanol which is produced on fermentation of sugar, is used for production of polyethylene, the polymer is referred to as bio-PE. Bio-PE has almost similar properties as the fossil based PE. Though biobased, its production cost and *non-biodegradability* is the downside of bio-PE.

Biobased Poly(Ethylene Terephthalate) (PET) and Poly(Trimethylene Terephthalate) (PTT):

PET, one of the commercially most important polyester prepared by condensing terephthalic acid with ethylene glycol. Instead of terephthalic acid very often dimethyl terephthalate is used because terephthalic acid is nonvolatile and slightly soluble in most of the solvents whereas dimethyl terephthalate can be purified easily distillation.

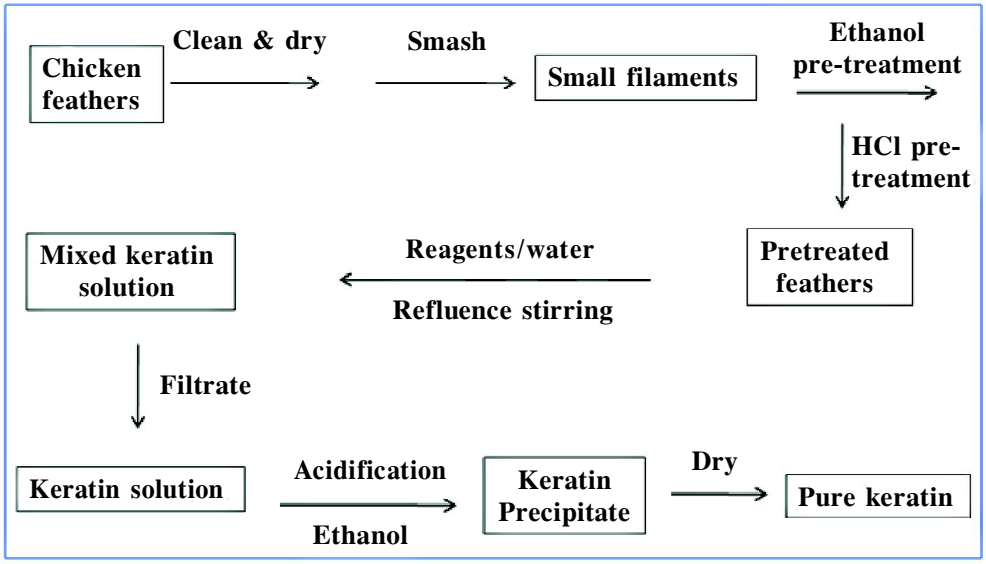


Bio-PET involves initially its monomer ‘ethylene glycol’ production from sustainable sources such as biomass. But now

people are trying to get biobased terephthalic acid (bio-TPA) too, for further improvement of sustainability. Bio-TPA can be prepared from iso-butanol[21], muconic acid[22], limonene[23] or furan derivatives[24–27].

A group of scientists are focussing on chicken feathers which are naturally abundant, and materials based on the renewable protein keratin, which is available there, might be biodegradable, and mechanically durable[28]. These feathers are basically waste products in the Poultry industry, causing environmentally disposal problems since they are not extracted properly and efficiently. Thus this waste, from both environmental and economic point of view, is used to process these resources into some useful materials which can exhibit biodegradability and/or recyclability as well as address the societal concern on waste disposal problems. Alpha and beta keratins are the two major classes in the protein family. We find alpha keratin form mainly in hair, whereas beta forms are present in nails and horns like harder substances.

Feather Keratin extraction



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As reported[29] the major part of poultry feather is the globular protein beta-keratin. The study reveals that hydrophobic amino acids content in feathers are more than hygroscopic amino acids thus it is partially hygroscopic in nature. Synthesis of glycerol-plasticized feather keratin films cross-linked by dialdehyde starch[30] were reported. The solubility and moisture content of the films was reported to decrease with increase in dialdehyde starch amount, whereas the tensile strength and water vapour barrier property decreased first and then increased.

Normally we can melt any plastics and mould them easily into required shape. But in the case of protein in general it is very difficult to get it into liquid, even if it happens irreversibly it may deform protein in this process. Many factors help almost all proteins to fold appropriately and thus assume a specific shape. Keratin till now looks not a good substitute for plastics, because of its brittleness i.e. easy to break.

Drawback of Bioplastics

(i) Starch based bioplastics are normally hydrophilic i.e. having high moisture sensitivity, low water stability and have high glass transition temperature.

(ii) Protein based bioplastics are hygroscopic and stiff and brittle due to extensive intermolecular interaction between protein chains.

Conclusion

The emerging areas for bioplastics are agricultural mulch film, shopping bags, consumer packaging materials, fishing line and nets, various sanitary products, coated paper, silage wrap etc. There are some modifications- improving biodegradability for certain environments, metallization to provide better barrier properties, addition of SiO_2, carbon fibre or other metals to increase thermal conductivity, specialized enzymes to enhance production- still required. Due to the belief that biodegradable plastics will decompose quickly, a possible increase in the incidence of littering may pose some adverse environmental risks

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because still most of the bioplastics need adequate composting facilities and/or anaerobic digestion facilities to degrade it.

Overall, even though bio-plastics are generally more expensive than regular plastic, the variety of uses and benefits could outweigh the cost. It cuts down the municipal waste, reduces greenhouse gases and is environmentally friendly. Hopefully with developing technologies, these benefits will improve and the cost will be competitive in the market and in the distant future robust interest in a sustainable society will reduce the dependency on conventional petroleum derived plastics.

** Picture Courtesy: https://executive.mit.edu/course/strategies-for-sustainable-business/a056g00000URaZPAA1.html

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