POWERING PROGRESS THROUGH PLASTICS

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BIO POLYMERS

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- Biopolymers or sometimes called as ‘green polymers’ broadly represent polymers produced from renewable resources.
- These polymers can be bio degradable as well as non biodegradable.
- Thus, ethylene made from ethyl alcohol and polymerized subsequently can still be called as bio polymer. This, however, is not bio degradable.
- Different biopolymers can be: polyesters, poly ether esters, polyamides, polyester amides, polyurethanes, polysaccharides etc.

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- **Historical:** Need for ‘bio degradable’ mulch film originated in USA to avoid the cost and efforts of removal of used mulch film.
- Polyethylene films were prepared by mixing up to 40% of bio degradable ‘additive’ such as starch, cellulose or lignin with polyethylene.
- The film did ‘degrade’ into powder in the field. The mechanical properties became progressively poor due to ‘degradation’.
- Essentially, microbes in the soil consumed starch and left behind the polyethylene.

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- A legislation or ‘standard’ was being developed so that it would become mandatory for farmers to use such ‘bio degradable’ mulch films.
- European scientists and perhaps farmers analyzed the residue and found that molecular weight of virgin polyethylene used for making the mulch film and the residual polyethylene was almost same.
- The legislation and so called ‘bio degradable’ mulch film did not succeed.

Introduction

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- One of the reasons for the developments in bio polymers is the increasing burden of non degradable wastes generated by the society.
- These wastes are affecting soil, aquatic life and also the birds as well as animal kingdom.
- Government initiatives have been to follow: reduce, reuse, recycle, incinerate or landfill.
- The composting is the cost effective and easy means to treat the organic wastes.

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- **Definition of bio degradability:**
- According to DIN 54900 – 2 (1998) is given as: the disintegration and subsequent metabolization of organic material under aerobic or anaerobic conditions through microorganisms to carbon dioxide / methane, water, mineral salts, and biomass.

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- Bio degradation process depends upon external conditions:
- (a) under aerobic conditions bacteria and fungi are involved and gaseous product is carbon dioxide,
- (b) under anaerobic conditions only bacteria are involved and the gaseous products are methane and carbon dioxide.
- Under aerobic conditions products of disintegration should be carbon dioxide and water.

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- Anaerobic conditions are similar to bio gas generation. The product of disintegration should be predominantly methane.
- Presence of microorganism is of course implied in both the processes.
- The residue of disintegration should be non toxic. Thus if catalyst is added for bio degradation, it should not leave behind materials like, mercury, lead, arsenic, chromium or similar metals.

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- Certifications such as **EN 13432, AQSTM 6400, AS 4736. GreenPla, or ISO 17088** further specify that a material is bio degradable if it bio degrades to 90 % or more in six months (aerobic conditions similar to composting) or to fifty % within two months (anaerobic conditions similar to bio gas plants).
- Many of spurious plastics are trying to enter Indian market as ‘bio degradable’.

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- Some industries test the ‘master batch’ containing additive or catalyst and ‘show’ that plastic degrades to more than 50 %. They do not test the film.
- Some industries are adding additive to the level of 5 % or less and claim that the resulting film is bio degradable.
- **If the polymer disintegrates into low molecular weight polymer but does not fully disintegrate into harmless products, the impact on environment is much more detrimental.**

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- Such bio degradable materials would lead to producing micro plastics.
- The fine powder can be air borne affecting the lungs of human beings, animals and birds.
- If water borne, the micro plastics will create harm to aquatic life like fish and could enter human diet.
- If the micro plastic powder mixes with soil, the fertility of soil can be endangered.
- It may be better to use non degradable plastic rather than using such spurious products which are more detrimental to environment.

General Characteristics of bio degradability

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- The bio degradability depends upon the morphology of polymer. Natural materials such as proteins, cellulose and starch degrade in biological system by hydrolysis of the molecule.
- The amide -, ester -, or urethane groups are hydrolysable. The main structure should have C – O, C – N, and C – C bonds.
- Water solubility is desirable and helpful.

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- Since most synthetic polymers are not water soluble, the degradation is effected through enzymatic, thermal, or photolytic disintegration.
- If oligomer or monomer is water soluble, the metabolization takes place inside the microorganisms.
- Affinity of polymer for water plays important role.

The factors favoring the degradability

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- **The factors which favor the degradability**:
- Low molecular weight
- Larger surface area as in thinner films, and
- Water solubility or higher hydrophilicity.
- The amorphous and flexible chain polymers degrade faster.
- In terms of chemical nature, the decreasing bio degradability is: ester> amide> ether> urethane.
- The aliphatic polymers degrade faster than aromatic polymers.

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- In a semi crystalline polymer, the amorphous portion degrades faster than crystalline portion.
- The stiff structure of polymer backbone (like benzene ring with para substitutions) is difficult to degrade.
- The low melting point polymers degrade faster. If the end use temperature is higher, the polymers degrade faster.
- All these factors have helped to develop some commercial bio degradable polymers.

Some commercial polymers and their characteristics

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- The polymers which could make some impact commercially could be:
- A) Poly Lactic Acid, PLA
- B) Poly Hydroxy Alkanoates, PHA,
- C) Poly Capro Lactone, PCL,
- D) Poly Butylene Succinate, PBS, and
- E) Poly Butylene Adipate – co – Terephthalte, PBAT.
- F) The other co polymers such as Poly Butylene Succinate – co – Terephthalate, PBST, a copolyester similar to PBAT.

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- The developments in bio degradable polymers:
- The good bio degradability but poor mechanical properties and /or high cost can hamper the development on a commercial success.
- In addition, thermal stability during processing should be good. The additives also need to be bio degradable or enviro friendly.
- Good bio degradability of PLA and good mechanical properties of PBAT are combined in a commercial blend of PLA and PBAT.

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- Most bio polymers are expensive. The cost could be 3 to 4 times the cost of PP or polyethylene.
- Most efforts are towards blending the expensive polymers such as PBAT with starch, cellulose, wood duct or waste jute to the extent possible for the given application.
- The market penetration rate of bio degradable plastics is as low as 0.1 to 0.2 %. However, based upon the market surveys, it is expected to grow at more than 10 % annually.

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- **Some characteristics of biopolymers:**
- PLA has good tensile properties but low elongation at break. It has lower modulus and ductility.
- PBAT has better ductility and elongation at break. Therefore, the blend of these two polymers has been widely used for flexible packaging applications.
- In flexible packaging antimicrobial additives enhance the shelf life of film as the growth of microorganism is prevented.

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- Agricultural mulch film is a much bigger market for the bio degradable plastics.
- Suitable grades of PLA for thermoforming, fibers and molding are being developed.
- PLA and PBAT are commercialized.
- PBS and PBST are being market tested.
- PHB and PHV are set to enter market by 2019/2020. World production, however, only 100,000 tons per year.

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- Blends of PLA, PBAT, PBS, PHB or PHV with thermoplastic starch have a good market potential.
- PCL is produced by ring opening polymerization of ε – caprolactone. It is used in durables such as adhesives or poly urethanes. Low melting point and flexibility are good points but cost is high.
- High cost has restricted growth of PBS.
- Production of succinic acid from bio waste could be helpful in reducing cost of PBS,

Applications and Developments

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- **Mulch films:**
- This market is the most appropriate.
- The degradation studies on field has been measured. The major polymer is PBAT, PBST and blends with PLA.
- The field testing of mulch film for strawberries and pineapple. The films degraded and lost mechanical strength after 8 to 10 weeks.
- The complete bio degradation occurred within 4 months.

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- Interesting study was made to prepare light conversion films.
- The uv light is converted into blue or red which increases the yield of crop.
- The additive is rare earth complex. (salts of Europium(III), namely complex with α – thenoyltrifluoroacetone and tri phenyl phosphine oxide with europium, EuTT.)
- If antimicrobial additive is added, the degradation time can be increased.

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- Blend of PBAT with PLA degrades faster than PBAT alone.
- PHB degrades fastest.
- By adding a compatiblizer in a PBAT/PLA blends, tear strength of film increased.
- By adding starch, the mechanical properties are reduced but cost also is lower.
- The different bacteria have different effectiveness for the degradation.
- All films degraded completely in the soil.

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- **Packaging films:**
- Reinforcement is achieved by blending nano clays, nano CaCO3 and to a lesser extent by nano starch.
- Anti microbial additive can delay the onset of bio degradation time significantly. One bio based anti microbial additive, Nissin – a polypeptide, has been tested.
- Thermoformed glasses/cups:
- A glass from PLA has been thermoformed for cold beverages. The results are encouraging.

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- Cups for fruit juices, cut fruit pieces etc have been tested successfully.
- For hot beverages, DPLA (and not LPLA) is found suitable.
- Additional tests need to be made for printing, transparency, processing instability of compostable materials currently available.
- Use of vegetable oil based plasticization is also studied.
- Effect of tri block compatiblizer is encouraging.

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- **Grocery shopping bags:**
- Initially, this application was targeted by some super market chains in Europe.
- The mixing of these bio degradable polymers with other thermoplastics such as LDPE/LLDPE was found to be detrimental in recycling and also environment due to selective bio degradation.
- This market is depleting.

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- **Garbage bags:**
- Apparently the conventional carry bags can be replaced by bio degradable plastics.
- This may create more harm!
- Just like any other carry bag, these may also leak into oceans or in water source.
- These bags do not degrade in oceans.
- The fate of degradation of other organic waste in presence of these polymers has not been established.

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- The need for providing a separate composting facility may be necessary. This cost may be connected with EPR.
- The danger of spurious and look alike non bio degradable carry bags coming in place of more expensive true bio degradable bags will spoil the environment much more.

Conclusions:

- Bio degradable plastics have a good potential.
- The high costs of these plastics may become less if large scale production starts.
- ‘Degradable’ plastics resulting in micro plastic of fragmented PE or PP need to curbed as these could be real threat to the environment.
- A good scope exists for new biopolymers.
- Lot of engineering data on bio polymers is needed.

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