BIO POLYMERS

Presented By:

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

Affinity of polymer for water plays important role.
The factors favoring the degradability
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.
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
• 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 – Terephthalate, PBAT.
• F) The other co polymers such as Poly Butylene Succinate – co – Terephthalate, PBST, a copolyester similar to PBAT.
• 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.
• 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.
• **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.
• 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.
• 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
• **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.
• 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.
• 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.
• **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.
• 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 compatibilizer is encouraging.
• Grocery shopping bags:
  • Initially, this application was targeted by some supermarket 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.
• 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.
• 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.
THANK YOU