

PolCoPUS
Prof. Abhijit P Deshpande
Department of Chemical Engineering
Indian Institute of Technology, Madras

Lecture No -87
Biodegradable polymers II

Hello, welcome to the course on polymers we are in the week 12 where we are discussing polymers in the environment. In this course we have discussed the properties, the uses, we discussed various concepts related to it and we had a significant emphasis on sustainability also. So in this lecture we will look at some of the applications of biodegradable polymers, so that the emphasis remains on uses.

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The slide, titled "Applications and processing", contains the following text:

- Develop biodegradable polymers:**
 - can be processed with ease
 - exhibit good performance
 - are cost-competitive
- Organic recycling or bio-recycling;** as opposed to mechanical and chemical recycling
- Processing of biodegradable polymers**
 - Extrusion
 - Film blowing and casting
 - Fiber spinning
- Current worldwide market of biodegradable polymer: less than 0.5% of polymeric materials

And we will look at these applications by first looking at what are the key ideas which drive the development of biodegradable polymers. So general drive is towards developing biodegradable polymers which can be processed easily, because we require these polymeric parts in very large volumes the processing speeds, the processing costs and so in general ease of processing has to be there.

Of course they have to exhibit properties which are required for a given application and equally importantly they has to be cost competitive the feature of cost competitiveness is also sometimes addressed by policies given the overall emphasis on sustainability at a societal level and at the

larger governance structures, which are there quite often cost competitiveness is ensured by providing certain incentives and subsidies to many of these practices which may lead to overall sustainable practices.

And so generally the emphasis with the biodegradable polymers we could say is on organic or biorecycling, so recycling is still the norm but the recycling happens by integrating polymeric materials with the overall bio geochemical cycles and the emphasis on mechanical and chemical recycling will be reduced therefore and the general techniques which are used for making objects out of biodegradable polymers essentially remain the same as what we have discussed earlier.

So extrusion of polylactic acid or film blowing using polyhydroxybutyrate and fiber spinning using polylactic acid so all of these are common techniques which are utilized and in fact one of the key issues associated with the biodegradable polymer is the use of these processing techniques and the advantage that polyethylene terephthalate or PE polyethylene gives in terms of their ease of processing sometimes cannot be matched by these polymers.

And lot of effort is also going on to understand the rheology of these polymers can we add few other things, so that the rheology improves and then processability improves. So generally lots of these challenges are being addressed while we have now more and more use of these biodegradable polymers. If you look at the current numbers the overall use of biodegradable polymers is very small it is less than 1% and in fact 0.5%.

And thereabouts in terms of what the overall amount of biodegradable polymers which are being used compared to the complete polymeric material usage that we have.

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Applications of biodegradable polymers

Most promising applications

Starch:

- Key challenges
 - Processing ease and optimum performance
- Applications
 - shopping bags, disposable domestic utensils
 - agriculture - films
 - automotive industry: interior parts
 - medicine - bone cement, drug release films
 - foam

Poly (hydroxybutyrate), PHB
poly (hydroxyalkanoates), PHAs:

- Key challenges
 - Cost of PHB polymerization / production
 - Transparency and toughness
- Potential applications
 - oxygen barrier films
 - biomedical devices
 - blends for packaging



So there is significant scope for moving towards more and more biodegradable polymers, so let us look at how the current products made out of biodegradable polymer? What are they made of and what products are being made? So if you look at starch based materials for example, the key challenge here is processing and also optimum performance quite often starch film may be brittle and so many of the film applications we want flexible transparent film.

So can that be as achieved using starch and can film be made at the same rate that currently many of polyethylene or other polypropylene other packaging films that we make. But many of these questions have been addressed to a limited extent and therefore we have seen that starch based shopping bags are there are a lot of domestic utensils which are available in the market. Agriculture which is where mulch films are used to try to manage the environment under which the plant growth happens there also starch based materials are used.

Even in fact interior parts in automotive sector, medicine use and also styrofoam instead of styrofoam can we use starch based form. Because styrofoam is a large again component of plastic waste management issues that we face and so form made out of starch is also a promising application which already is being done to a limited extent. If we look at polyhydroxybutyrate, the key challenge still remains the cost.

Because it is a microorganism produced polymer the rate at which in the amounts that can be produced still leads to the cost of PHB, being very high and the other thing of course will be in terms of properties can it be as transparent and as tough as the material that it is trying to replace. But it is still being researched quite a lot there are very few commercial exploitation of PHB but lot of promise based on its availability as a microorganism based polymeric material.

And its properties are also quite promising but cost remains high, so therefore the potential applications could be in oxygen barrier films in biomedical devices or blend it with other sets of polymers so that we can arrive at effective packaging materials.

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Most promising applications

Poly (lactic acid), PLA:

- Key challenges
 - Control on stereo-chemistry of PLA - L and D enantiomers → Glassy and semi-crystalline polymers
- Applications
 - nonwoven materials (fiber ⇒ PLA)
 - sanitary napkins, diapers, cleaning tissues, clothing
 - packaging materials
 - thermoformed food containers
 - bottles
 - biomedical devices
 - automotive parts
 - electronic devices

So let us look at the other polymer which is very commonly used these days polylactic acid and this is again a polymer which is not produced by microorganisms or animals it is actually a bio based polymer. So the ingredients and the monomers can come from renewable sources but it is a synthesized polymer and the key challenge of making polylactic acid is to control the stereochemistry or the enantiomers which are present there and these influence whether the material is amorphous or semi crystalline.

And so properties get significantly impacted based on the presence of what is the stereochemistry along the macromolecule. However the processing capability of polylactic acid also depends on the overall macromolecular conformations which are possible in because of the stereochemistry.

So, generally different additives are added to polylactic acid to improve the processability. But this is being used to quite significant extent as a fiber form in non woven materials.

So this is PLA fiber is quite common in terms of making different types of products which are you can see all disposable products such as sanitary napkins, diapers and tissues it is been also used as packaging materials, food containers and bottles and again applications where we may not use it in the film or fiber form but more as a product which is molded and shaped. So whether it is electronic or automotive or biomedical again the application is keeping in mind the overall biodegradability aspect of polylactic acid.

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The slide, titled "Biodegradable polyesters", lists the following properties and examples:

- $T_g \sim 30^\circ\text{C}$; $T_m \sim 115^\circ\text{C}$
- An example: BioPBS™ polymer based on renewable resources and compostable
- Mulch films, bags
- Thermoformed products
- Strength / strain at failure ~ LDPE
- Aliphatic / aromatic copolyesters
- Biodegradation of random copolymers faster than block copolymers
- Packaging

Chemical structures shown include succinic acid, 1,4-butanediol, and the resulting poly(butylene succinate) chain. A chemical reaction shows the esterification of succinic acid and 1,4-butanediol to form the polymer chain with the elimination of water. Another structure shows a copolymer chain with both succinate and terephthalate units.

So the other class of polymers which are common are polyesters and as we have seen polyesters have a natural tendency to get attacked with water present and then give us carboxylic acid and alcohol and so examples of this is poly butylene succinate or poly butylene adipate terephthalate in fact they form about 20% of the overall biodegradable polymer production. So they are quite significant one-fifth of biodegradable polymers which are out there in the world and this is basically data which is a few years old.

But it gives us an idea that these two polyesters are also quite important as far part of the components of the overall biodegradable mix which is out there in the market and you can see why the properties are similar in some respect to polyethylene, polypropylene the glass transition

is -30 for PBS and the melting temperature is 115. Basically PBS is arrived by again doing a standard condensation reaction between di-ol and di-acid succinic acid with butane diol.

And we get basically the polyester formation because of water coming in and out of the system and these are used as mulch films and bags and they also have a significant promise in terms of producing shapes which are thermoformed. So these are not flat shapes but at the same time they are not extremely complicated shapes which can be used as a stamping operation and thermoforming can be done.

On the other hand, the PBAT is a co-polyester so it in fact contains aliphatic and aromatic part of polyester. So you can recognize this and immediately figure out why PET for example, polyethylene terephthalate is non biodegradable even though it is polyester because of the presence of the aromatic group along PET the access of water the access of enzymes, the possibility of cleavage reactions, the possibility of assimilation all of that reduces.

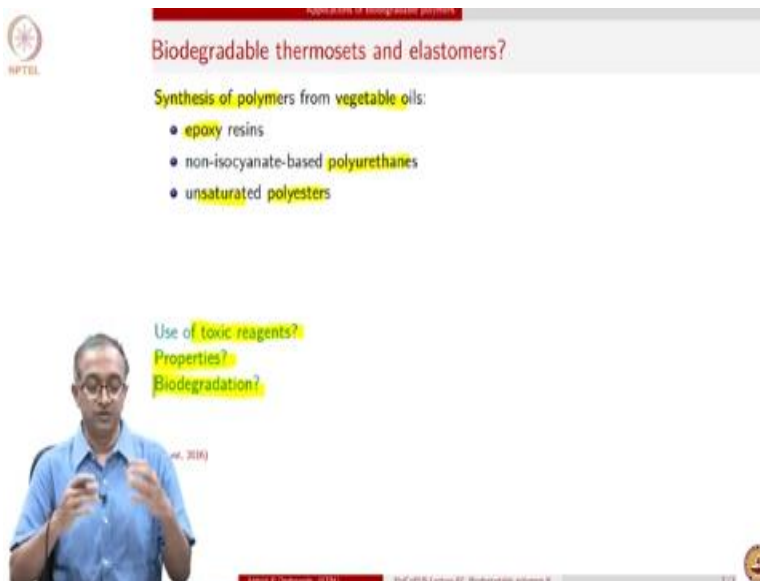
So the presence of aromatic group generally will lead a polyester away from bio degradation. On the other hand if you only have aliphatic polyester then you get only limited set of properties, so therefore these copolyesters are an attempt to make a copolymer which has appropriate biodegradation properties as well as appropriate mechanical and thermal response for the applications.

So therefore their strength and strain at failure is similar to polyethylene and biodegradation of random copolymers is faster than block copolymers because when you have blocks of poly aromatic entities what happens is access again to biodegradation is much less. But on the other hand if you have these aromatic groups as random monomers on the macromolecular chain then chain cleavage can happen wherever there are aliphatic chains and smaller molecules then can be assimilated by microorganisms.

And generally the PBAT is used as packaging applications so you can see that there are several examples of these biodegradable polymers and one thing you might have noticed in terms of the

processing techniques that I discussed in terms of molecular architecture that I discussed that these all belong to thermoplastic.

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So we will close this lecture by pondering little bit on what about biodegradable thermosets and elastomers, because we know that these two cross linked systems also form a significant usage of polymeric materials and the stability which is given by thermosets or the flexibility and damping properties which are provided by elastomers so they are very important for variety of applications.

So is it possible to think of biodegradable thermosets and elastomers and this still largely remains a research topic, there are of course degradable thermosets in which case we are not talking in terms of bio degradation but a thermoset which can be de-crosslinked and this we have discussed earlier also but however can we have a thermoset an elastomer which is completely biodegradable.

So one line of thought in this direction could be let us say synthesis of these kind of polymers such as epoxy or polyurethanes or unsaturated polyesters which are used in cross-linked polymeric systems can they be made out of a renewable source and during this process can we make sure that we use reagents which are not as toxic and we lead to a set of properties which are as good as the synthetic epoxy or synthetic polyester resins.

And finally can we ensure that they still remain biodegradable so many of the functional groups which are present in vegetable oil which make it a naturally biodegradable molecule can they be retained in the final macromolecule. So that chain cleavage and sematic access and biodegradation bio assimilation are all possible. So with this thought we will leave many of these are still questions to be addressed by our scientists and engineers to make polymeric materials more sustainable for their applications. So we will stop the lecture here, thank you.