Introduction to Polymer Science
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Lecture-42
Polymer Blends, Concluding Remarks

Welcome back, in this lecture and this will be the main last lecture for this course.

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I will briefly talk about polymer blends and then have some concluding remarks about the polymer science.

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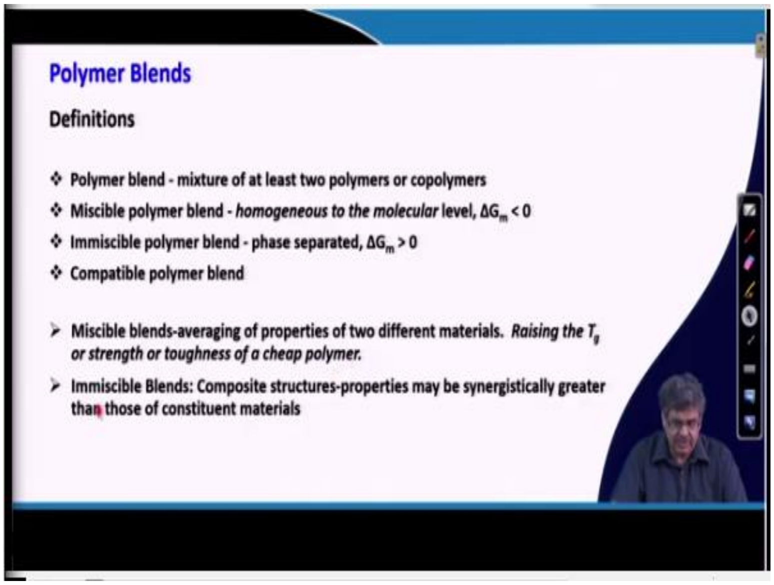

When you discuss polymer blends, it is basically a mixture of two or more polymers, which could be homo polymers as well as copolymers. So, polymer blends are the mixture of at least two polymers which could be homo polymers or copolymers as well. Now when these polymers get mixed in a homogeneous level or a homogeneous at molecular level we call this as miscible polymer blend and that happens when the Gibbs free energy of mixing is less than 0 or negative.

And when this gives me of mixing is positive then this polymer blend actually form a immiscible polymer blend where the different polymers form different separated phases. And sometimes these immiscible polymer blends are which actually have present in different phases, they can be kind of tied to each other. So, that they do not get separated farther by using some compatibilizer and which creates comfortablized polymer blends.

Miscible blend have averaging of properties between two materials for examples we are using two different T g in the polymers having to define T g. Then it will raise the T g of the lower component or it will raise the strength or toughness of a cheap polymer. So, sometimes miscible blends are created or to increase the strength or T g or the toughness of a cheap polymer by adding some other polymer.

An immiscible blends are a composite structure and properties are a synergistically greater than those of constituent materials. Sometimes deliberately immiscible blends or compatibilized blends are created. So, that the property or the performance of these blends is better than individual constituents.

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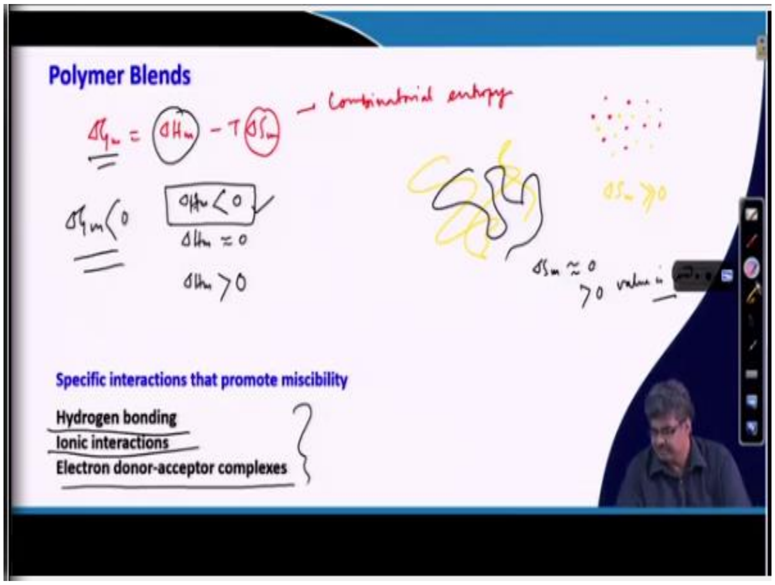

Now when we talk about thermodynamics of polymer blend, if we talk about delta G mix, we know delta H mix - T delta S mix. Now for a given temperature and pressure as we discussed in our lectures on polymer solution, this is combinatorial entropy which comes because of the change in conformation of the polymer molecules. Now when you mix two different small molecules, say you using molecules of different color invariably the entropy is mixing is positive.

Because there are many combinations possible I discuss these during derivation of Flory-Huggins equation. So, when we mix small molecules, invariably delta S mixture is much higher than 0. So, that is why unless there is a repulsive interaction between the molecules, mixing is always favorable for small molecule. But when you use large polymer molecules like this and we use some other color.

So, if you use two different polymer, because the polymers are large in size, the gain the value of this combinatorial entropy of mixing is low. They either very close to 0 or they are positive but the value is very low. So, the polymer - polymer miscibility is mainly determined the value of del H. If del H mixing is negative then miscibility is favorable is del H am is close to 0 then it is either miscible or immiscible depending upon the value of delta S same which depends on the molecular weight as well.

The higher is the molecular weight, the miscibility comes down because that the value of delta G is same becomes close to 0. Lower molecular probably will be better miscible sigma if we have delta m positive, then obviously they are not miscible. So, to have 2 polymer to become miscible with each other we should have delta H, am delta H mixing less than 0 which happens if there are strong inter polymer interaction, attractive interaction between these two polymer chain.

And that happens if we have like hydrogen bonding between polymer chains, ionic interactions or electron donor acceptor complex formation between polymer chains. If these things happened then there is strong attractive interaction between polymer chains. And that helps the value of del H becomes negative as a result delta G becomes negative and the polymers become miscible with each other.

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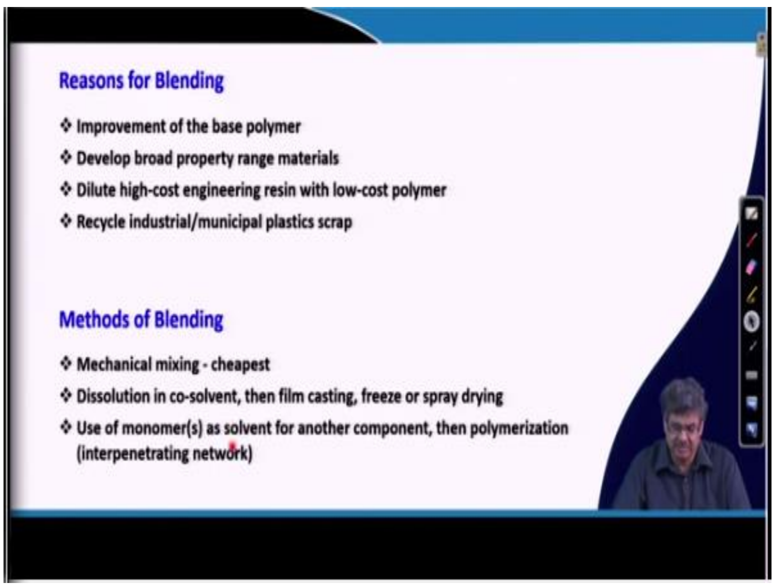

Now why should we blend, we discussed little bit in the first slide, because it improves the base polymer specially if the base polymer is a cheap polymer. Then we can add some other polymers to improve the performance of the base polymer. And it actually helps in developing broad range of property from same two polymer we can mix in different ratios to make different grades and basically have a different products. Obviously if we using two polymers have different costs, the blend cost will also vary but if require the final application does not require very high property.

Then we can use probably a cheaper polymer the blend with the higher cheaper polymer component and use that. So, basically we can actually use the blends to develop a range of material. And dilute the cost of engineering resin or with low cost polymer and it can help in recycling the municipal waste or plastic waste. The methods of blendings can be either mechanical mixing, which is the cheapest way of mixing or blending polymers.

It can be done by dissolving the polymers in a common solvent and then casting a flame or by freeze drying or spray drying but this is the most costly affair especially a use of solvent is also hazardous. And we can use kind of polymerization technique where the other polymer can be used as a solvent and we can polymerize the other monomer in presence of that polymer. So, it gives kind of a interpenetrating network but it is not a true sense of blending process because we are not mixing 2 polymers.

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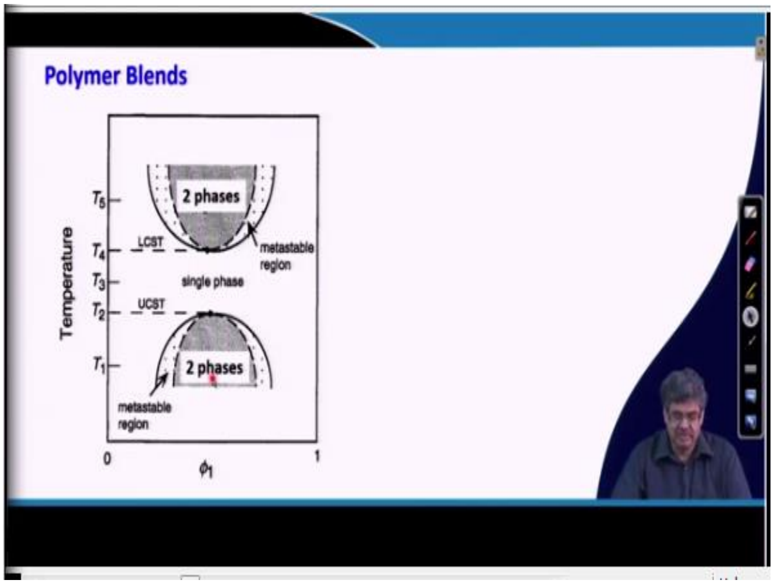

And this is a possible phase diagram, not necessarily each polymer pier will have all these LCST and different region. This is the total possible scenario which captured in this phase diagram. And this value corresponds to lower critical solution temperatures, which means below this temperature the 2 polymers become miscible and above this temperature depending upon the composition, it can remain either in immiscible or in immiscible phase.

And within this immiscible phase we can have a metastable region and a completely phase separated two regions. Similarly we can have another scenario where above a certain temperature, the polymers become miscible they have a single phase and these particular temperature is called upper critical solution temperature or UCST below which depending upon the composition either we can have a single phase or a two phase scenario.

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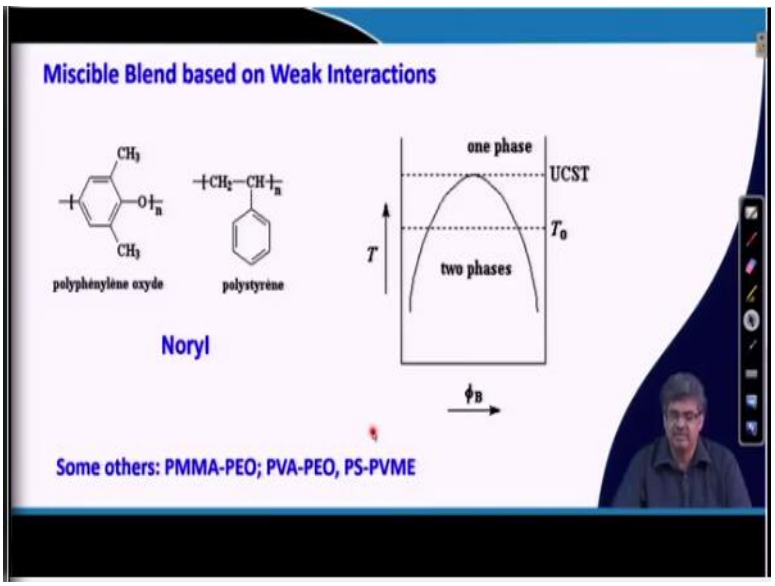

Some example of miscible blend with weak interactions like **miss** blend of polyphenylene oxide and polystyrene commercially it is sold by in the name of Noryl. And the other examples are like PMMA-PEO, PVA-PEO PS-PVME these are the example of miscible blend having weak interactions.

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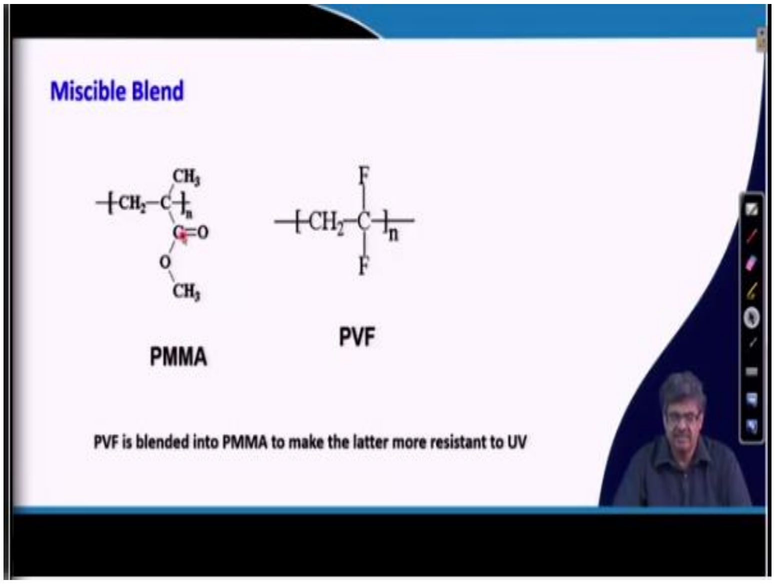

Other examples of miscible blend like PMMA and PVF, in this case PVF which is a costlier polymer which is blended into PMMA to make the UV resistant or PMMA higher. In this case, small amount of PVF is added to PMMA, so that the UV resistant PMMA becomes higher.

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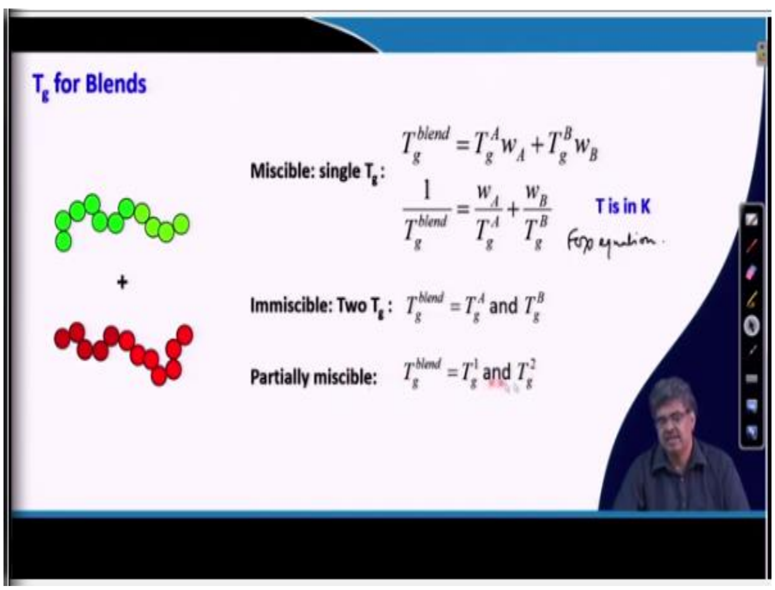

Now as we described earlier in this slide is basically repeating from my earlier lectures where for a blend, the T g is given by how these blends from their miscible property. If they are miscible there is a average single T g which is given by these expressions. And this is the most accurate equation by which can be used. And this is Fox equation, as I have mentioned earlier where these T g A and T g B are the T g for polymer A and polymer B respectively.

If they are immiscible then we get 2 T g's for individual homopolymers and they are partially miscible we still get 2 T g's but the T g's in this blend is different as I discussed earlier.

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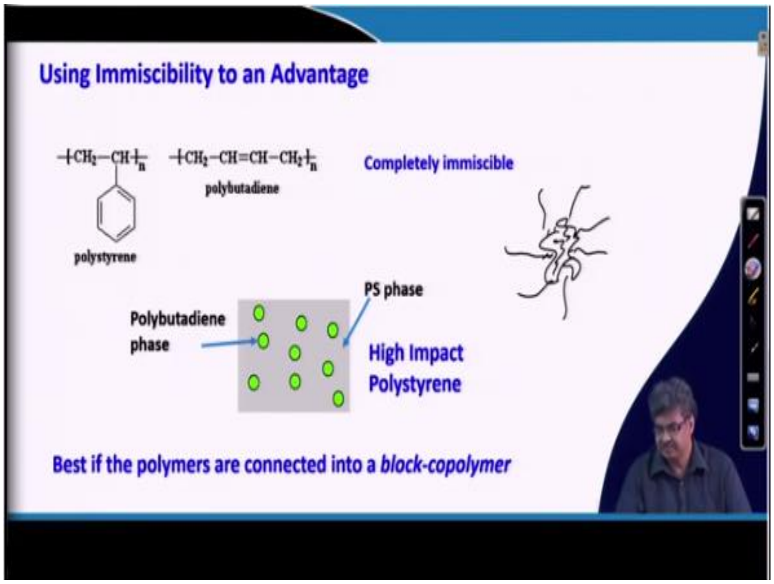

Now we can use this immiscibility to our advantages, for example polystyrene is a brittle polymer. Now to improve the impact behavior or ductility of polystyrene, this rubber polybutadiene rubber is added. Now if they were completely miscible then we would have a single phase and the impact property of polystyrene would have increases marginally because of presence of polybutadiene.

But because they are immiscible we can have polybutadiene added in the polystyrene matrix. And as a result this polybutadiene will phase separate and remain as a this type of phase separated. And we can use some compatibilizer to compatibilize these or we can basically have the covalent bonding between these phase with polystyrene might takes. As a result these polybutadiene phase will act as a impact modifier.

And as a result this blend of polystyrene and polybutadiene is a example of high impact polystyrene. It is best if we have these polymers, polystyrene is connected covalently with polybutadiene as a block copolymer. And that is generally done we made it our core polybutadiene core and from that core polystyrene, you basically make a polybutadiene core and there will be double bonds.

And from that core polystyrene are generated to make a core cell type polymers which will have high impact.

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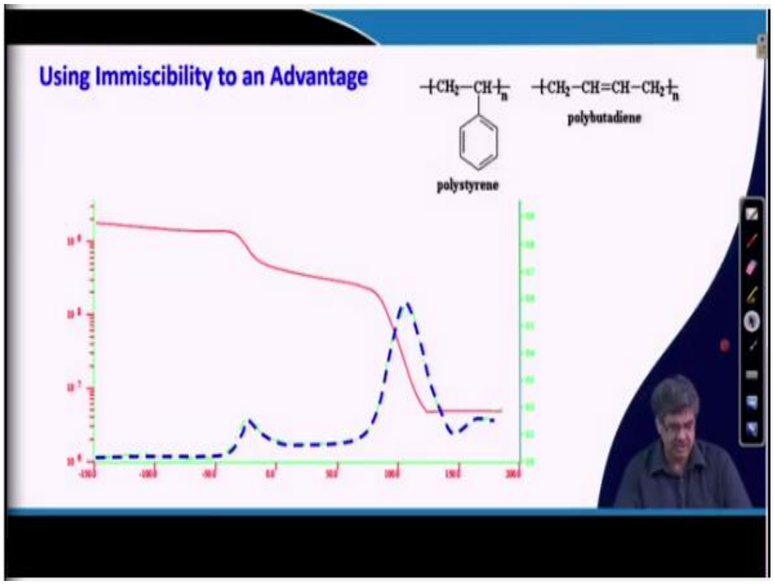

And if we do a DMA of this polystyrene polybutadiene sample, we can see that this is a T g corresponds to the polybutadiene phase and this is T g corresponds to polystyrene phase and this is tan delta. So, you can see there is a maximum here corresponds to the T g of polybutadiene and there is a maxima around little over 100 degree which corresponds to the maxima corresponds to the T g of polystyrene molecule.

So, we are plotting G in this case and this is G prime and this is tan delta. So, this is corresponds to T g of PS and these corresponds to T g of PB polybutadiene, this is tan delta. So, we now see that there is always a useful there is a reason why we wanted to make either miscible blend or a immiscible blend. It is not that always it is better to prepare a miscible blend with sometimes immiscible blend like the example shown here also improved the property of the base polymer, ok.

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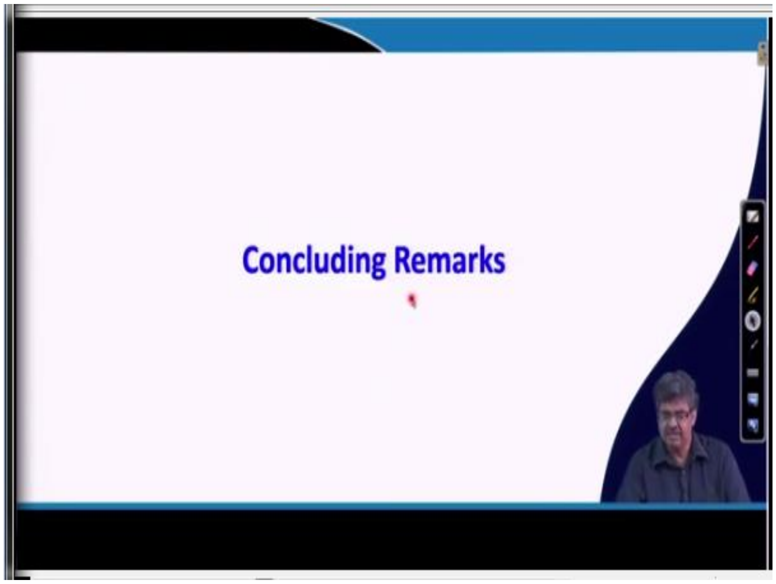

With this I will have some concluding remark about the polymer science.

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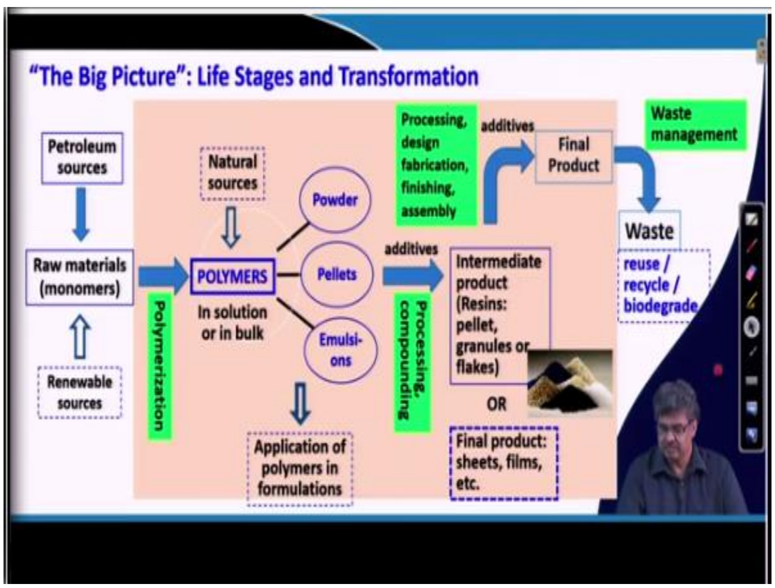

And if we go back and remember this slide I have shown few times this is the complete picture of life stages and transformation reactions starting from the source of the polymer monomers and polymer and then polymerization and then product. So, this is the part I have discussed during last all the lectures, the only part we have not discussed is about the source of the raw material and the waste management.

And in fact these are probably very important it is probably as important as this part as well. Now there was a concern about the raw material, most of the synthetic polymers are synthesized from monomers which are derived from petroleum resources basically oil, crude oil. Now that concern is basically reducing with day by day because of evolution of electric cars and electric vehicles which basically consume the petroleum products like oil most.

Because there is a demand of oil is slowing in that aspect. So, the concern of supply of monomers from those crude are actually coming down. In fact I was told by a one great scientist that, in fact there are enough reserves of oil to be supplied for many centuries to synthesize a synthetic polymers. So, this part is probably is not that concerning now, rather than it is mostly important to think about what to do with this polymer materials.

And most of the bad name of polymer materials are because of this bad management of the polymer waste. So, if we can actually do a most proper waste management, then the bad name of polymers are actually will not be there.

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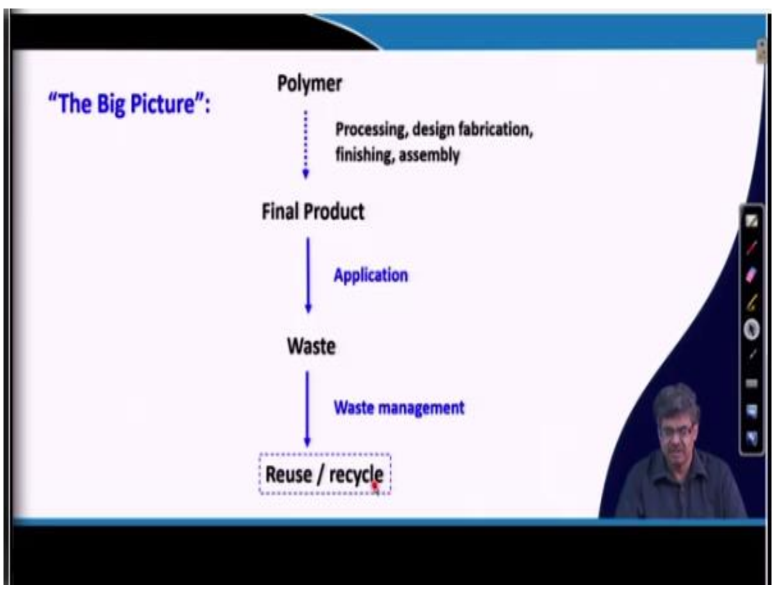

So, if we go back and look at again polymer actually gives you the final product using these steps. And then after the application wastes are generated and this is a very important how do we manage the resulting waste. And we should be either reusing this material or we should be recycling, that is the most important.

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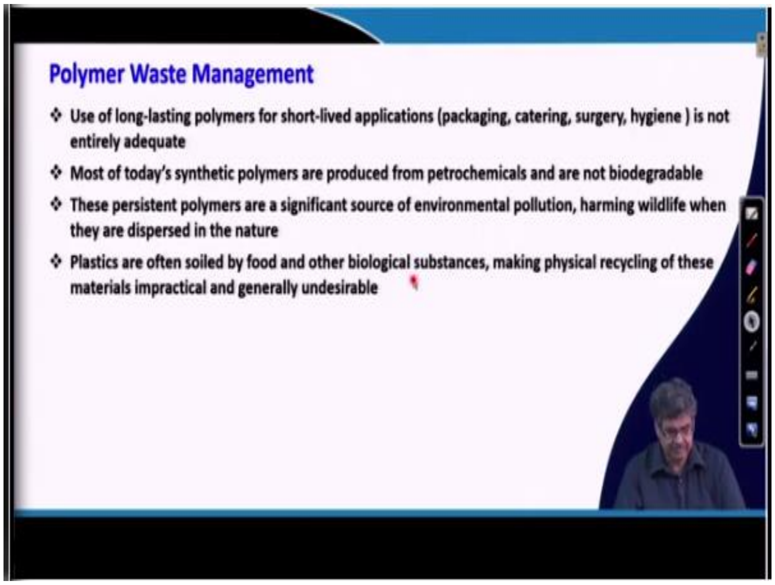

So, if we look at the polymer waste management, the most problematic aspect comes when use of long lasting polymers for short lived applications. Like packaging, carry bag and bottles, where this is a short lasting application, we drink water from bottle and throw it. Basically the application duration is very small but the life of the polymer is very large, so there actually is a main problem.

And most of the today's synthetic polymers are produced from petrochemicals and not biodegradable. So, these persistent polymers are a significant source of environmental pollution and they harm actually wildlife when they are dispersed in nature. Like in seawater we always see bad picture of plastic bags and plastic bottles are lying on the sewage and or floating on the sea water and so on which is harmful for wildlife or sea life, aquatic life as well.

And plastics after use are often soiled by food and other biological substances, as the result, making physical recycling of these materials are kind of impractical and generally undesirable. So, if we use a bottle and for storing a juice or some other thing and then these bottles or these packets, they actually gets contaminated with the food or the substances which are used for which came in contact with this material as a result physical recycling is very difficult.

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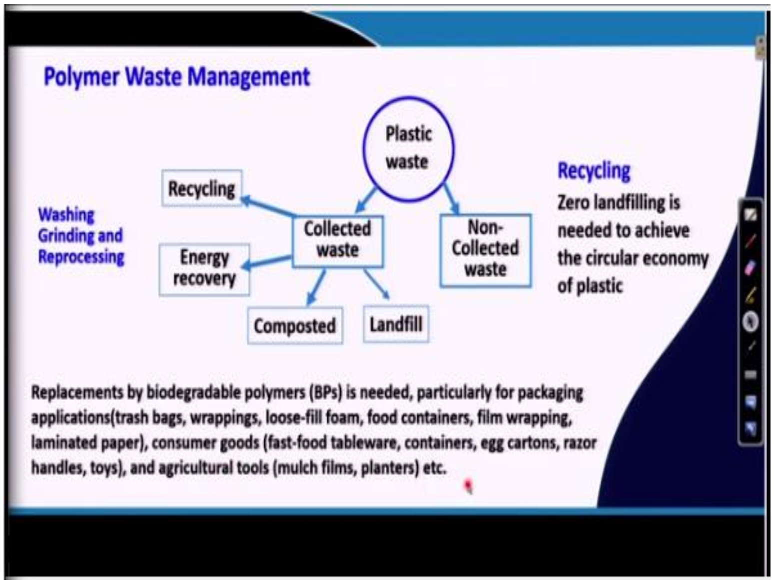

So, what we generally is done with the waste, there are mainly two types of waste when, what is the majority you know are collected waste. They are collected from waste bins and then either recycled or they are incinerated and used as a energy source or they can be compost using micro bios to further use as a monomer resource back to polymer industry or as a fertilizer or if none of these can be possible.

Then they can be basically put in a landfill, so that they can be less harmful to the environment. The most problematic comes is the non collected ways like those plastics, carry bags or bottles which are thrown away in some parts where these are not collected those are the pictures we see from you know different sources. So, if we can reduce these non collected waste and that can be only done if all of us who are using plastics, we can actually dispose the plastics in proper way.

So, that when if a person collectivities is done these plastics waste can be collected and either of these 4 processes can be applied to this waste, so that the pollution or hazard is minimized. For this non collected waste it is actually better if we can use biodegradable plastics or biodegradable polymer. Then even if we do not collect this material probably it will not do as much as harm if the polymers were not biodegradable.

Now after collecting the polymer waste, for recycling or other process to happen with these collected waste need to be washed. And if they are used for recycling then it has to be grinded and reprocessed for making further product which is also cost effective you know costly affair. As a result, there is always the economic challenge of polymer recycling unless we can reuse a find a high cost application then it becomes always challenging.

Because these polymers they are not based polymers, they are not only 100% pure water. As I discuss, they will have additives, they will have fillers and in result they cannot be used for the applications, original application. Like if one plastics or polymer were used for a water bottle then that cannot be recycled back again for making a water bottle because it presence obvious additives and other contaminants.

Hence these recycled plastics are generally used for low end applications non food or non health related applications. And generally when you see a black polymers like this black bin, dustbin bags these are generally are synthesized from recycled plastics. So, zero landfilling is the needed to achieve circular economy of plastics. So, if we whatever we can collect the plastics from waste, they can either be recycled back to the system which will be only possible.

We have a zero landfill and zero non collected waste, then we can have a circular economy for plastics. So, replacements of biodegradable polymers is needed particularly for packaging applications, trash bag, wrapping, loose fill foam, food containers, film wrapping and other places.

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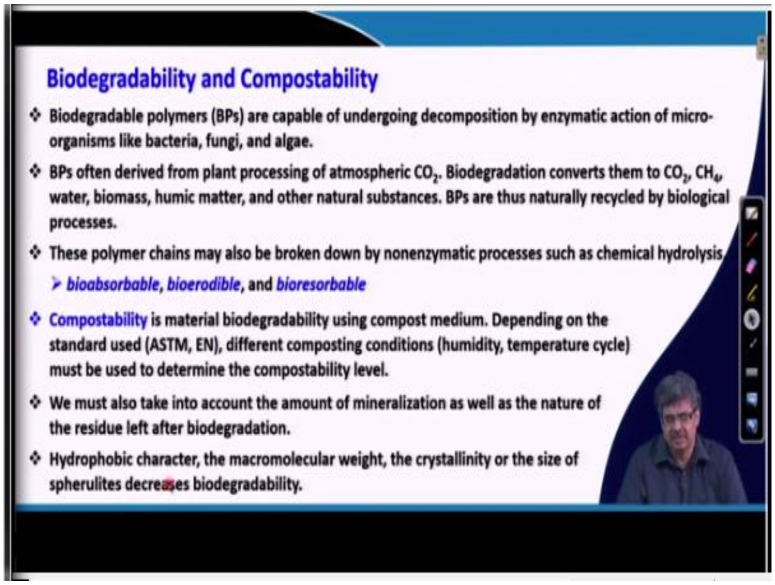

So, we should discuss about biodegradability and compostability. Now biodegradable polymers are capable of undergoing decomposition by enzymatic action of microbes on microorganisms like bacteria, fungi and algae. Now these biodegradable polymers often are derived from plant processing of atmospheric oxygen. So, plants actually processed as basically they collect the CO 2 and from which the biodegradable polymers are actually synthesize.

Biodegradation is the process which convert back, these biodegradable polymers to carbon dioxide, CH 4, water, biomass, humic, matter and other natural substances. Thus biodegradable polymers are naturally **cyclic** cycled by biological processes. These polymers chains may also be broken down by non enzymatic processes such as chemical hydrolysis but these are not very commonly encountered by normal for plastics.

Because if they are anyway get hydrolyzed in presence of some chemicals or some non enzymatic process, then they are usefulness also will come down. Because during use also it will hydrolysis and become the property degrade. Sometimes these biodegradable terms are replaced with bioabsorbable or bioerodible or bioreobsorbable materials these all these have similar meaning.

Compostability is a material biodegradability using compost medium. Depending on the standard use like ASTM standard or European standards different composting conditions like humidity, temperature cycle must be determined or it must be used to determine the compostability level. So, to finding out the compostability of a polymer sample, there has to be you know some standard conditions to be applied which is given by the regulatory agencies.

And we also must take care about the amount of mineralization happen and what is the nature of these residues after biodegradation? Generally, the polymers which have hydrophobic character or having a high molecular weight and higher crystallinity they actually degrade to a lower extent. Because you know during compostability water is a factor, what if the polymers do not come in contact with water? Then obviously compostability or degradability becomes lower and lower.

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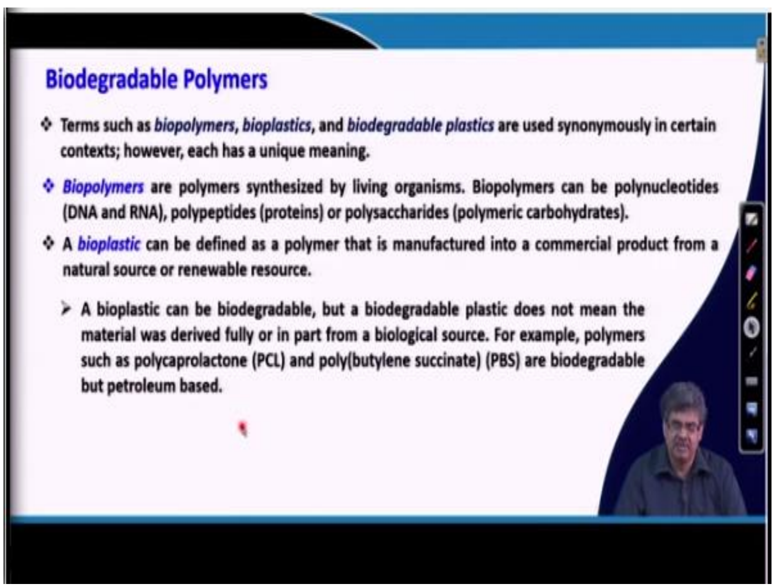

Sometimes these terms like biopolymers, bioplastics, biodegradable plastics are used synonymously in certain contexts but each has unique meaning. For example, biopolymers are the polymers synthesized by living organisms. They can be polynucleotides like DNA, RNA or polypeptides, proteins or polysaccharides, polymeric carbohydrates. A bioplastics can be defined as a polymer that is manufactured into commercial product from natural source or renewable sources.

So, there is a little difference between biopolymers and bioplastics. A bioplastics can be biodegradable but a biodegradable plastics does not mean the material was derived fully or in part from biological sources. For example, polymers such as polycaprolactone or poly butylene succinate, they are partially biodegradable but they are not sourced from a natural source or biodegradable sources they are synthesized from petroleum products.

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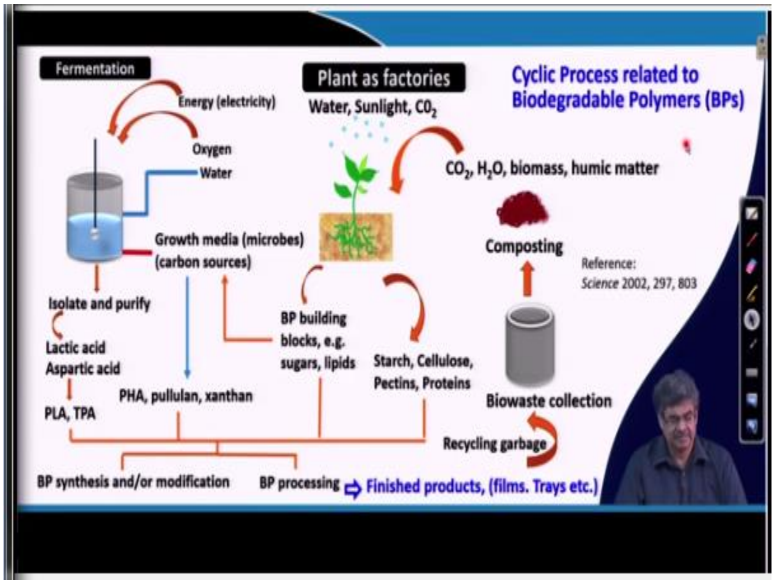

So, this gives a cyclic process of related to biodegradable polymers and basically plant take with the help of water, sunlight and carbon dioxide, they produce raw material for biodegradable polymers. For example they produces a starch, cellulose, pectin they can directly be used as a biodegradable polymers for mating products. They also makes building blocks for making biodegradable polymers like sugars and lipid.

So, which can be polymerized to make biodegradable polymers, they gives these sugars and lipids which can be actually using biotechnology is called root like using microbes. They can convert these raw materials to polymers like polyhydroxy acrylates, pullulan, xanthan. So, using microbes they can be directly converted to biodegradable polymers or they can be fermented to some monomeric products.

Like lactic acid, aspartic acid which can be used as monomer for making biodegradable polymers like poly acrylic acid or thermal polyaspartate and so on. So, there are 4 different ways we can synthesize biodegradable polymers but the source is has to be from plant, they can directly produced like biodegradable polymer, they can produce monomers which can be converted to biodegradable polymers.

They can produce monomer which can be converted to biodegradable polymers using microbes or they can be converted to other monomers by fermentation process which can be again polymerize to produce biodegradable polymers. Once the polymer and produced they can be use to make different products and after using those products they can be recycled back. And by composting, we can get back this raw material which can be against either be used for the fertilizer or for the agriculture applications. So, this is gives you a cyclic picture for biodegradable polymers.

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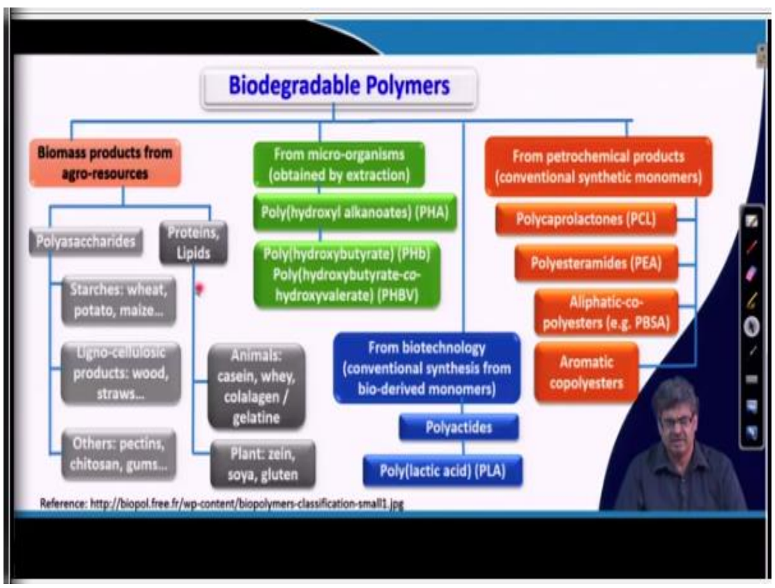

These are the four types of biodegradable polymers we described and there is a name corresponds to that, you can look at this chart in detail. In addition to the four biodegradable polymers, which we discussed in the last slides. There is some synthetic polymers like polycaprolactone, polyester, amides especially aliphatic polyesters, they are also either partly or fully in biodegradable.

So, in effect we talked about four different types of biodegradable possible in last slide. And we can also have few synthetic polymers which are biodegradable.

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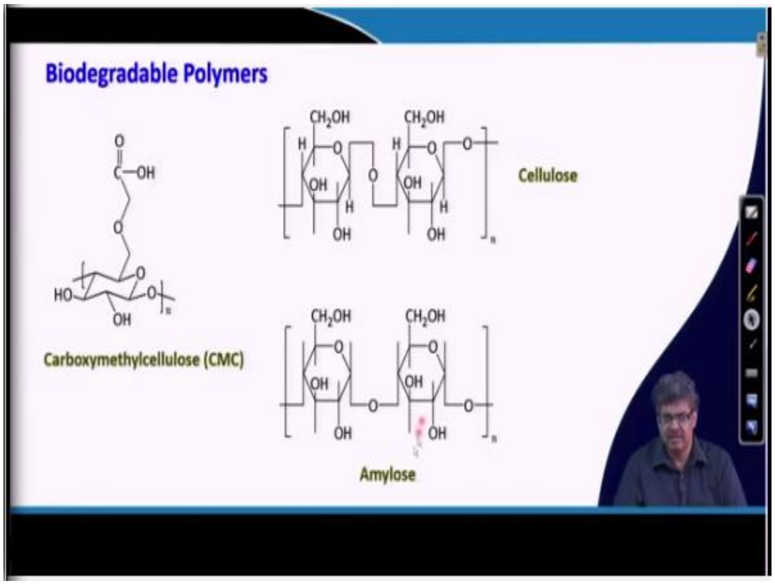

These are some of the chemical structures of biodegradable polymers, cellulose, amylase, carboxymethylcellulose.

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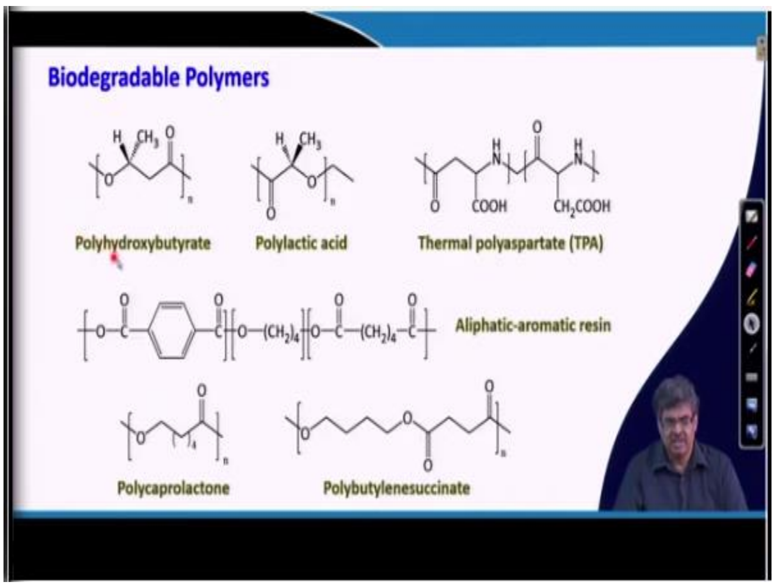

Polyhydroxybutyrate, polylactic acid, thermal polyaspartate, this is some synthetic polymers like polycaprolactone, poly butylene succinate, they are either partly or fully biodegradable.

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Let me conclude by giving you some directions about or some idea about Indian plastics industry very briefly.

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Company	LDPE	LLDPE	HDPE	PP	PVC	PS/ EPS	PET	2019-20	% SHARE
Reliance Industries	205	445	500	2700	725		970	6545	41.46
Indian Oil Corp		225	475	600				2000	12.67
Haldia Petrochemicals		210	500	390				1100	6.97
GAIL (India)		350	570					920	5.83
HPCL Mittal Energy				440				440	2.79
IVL Dhunseri Petrochem							480	480	3.04
Supreme Petrochem						340		340	2.15
Finolex Industries					270			270	1.71
Chemplast Sanmar					290			290	1.84
LG Polymers India						130		130	0.82
Ineos Styrolution						105		185	1.17
ONGC Petroadditions Ltd		360	700	340				1400	8.87

And these are the main companies in India of which produces plastics starting from Reliance industries and Indian oil corporation or their petrochemicals. And the products are listed here, and then their amount and the percentage of share also as mentioned in this. So, this is just to give you the companies which basically makes polymer in our country.

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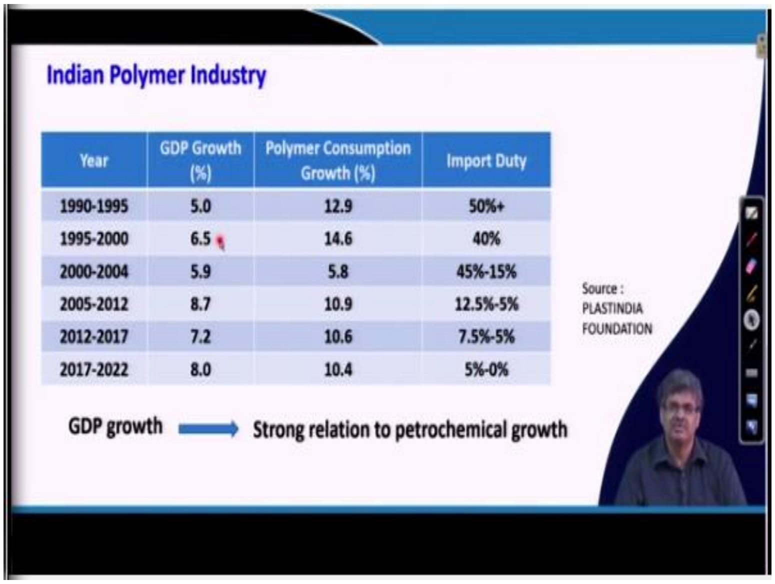

And there is a steady growth as our GDP grows steadily with time the growth of polymers also increasing steadily as time. So, GDP growth has a strong relation with plastic growth.

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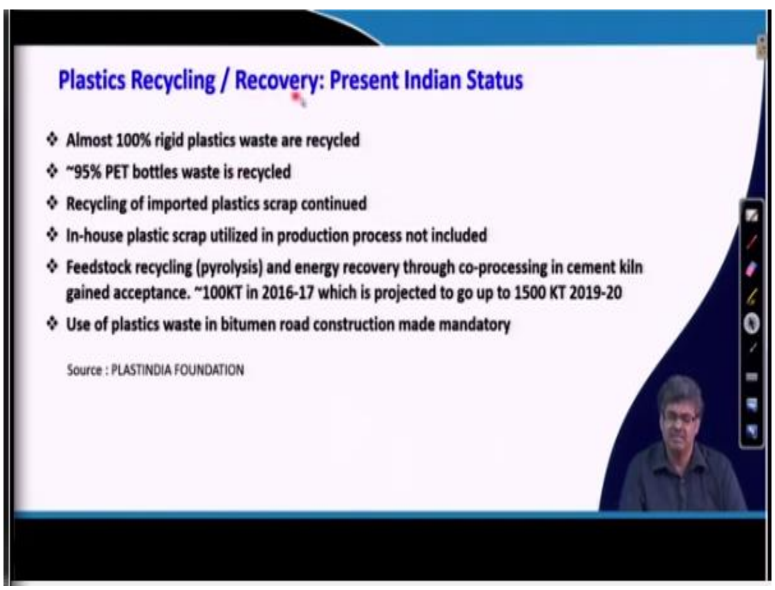

The situation of plastic recycling and recovery in India is not very bleak. In fact almost 100% of rigid plastic waste are recycled and for example 95% PET bottle waste are recycled. And so basically the regulatory agencies are trying their best and in fact the situation is not that bad you know. Only the single use plastics are this like packaging materials which causes most concern. So, if we as a consumer take some responsibility to discard those packaging materials in a proper way then the problem of plastics will not come.

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So, in summary huge growth opportunities in India for plastics due to low per capita consumption compared to other developed countries in world. Flexible packaging industry poised for strong growth and insulated from current economic scenario due to huge and diversified consumer base. And plan infrastructure projects are driving growth in India and these are ably supported by current and upcoming domestic capacities.

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Now I will give a concluding side that **in** as a polymer scientists or a polymer chemists which should not be you know having any doubt about the future of polymers or plastics. For example look at this situation**,** now the pandemic situation and all these PPE's which are being used by doctors and nurses or you know look at what? These all these are made from polymers.

We are talking about the medical equipment, medical disposables like syringes and gloves and all these things, they are all made by polymers. So, unless we basically have polymers, it is not possible. So, although polymers have kind of bad name because of their environmental hazards but as I said once more earlier also, I am saying once more this is responsibility for the consumers like us to discard the polymers or plastic materials what we using properly?

If we discard properly, then we will be able to solve this problem of plastics waste. With this let me conclude and I hope you enjoyed this course of introduction to polymer science. In case you have any question, you are free to ask me over phone or you can send me an email, my email address is available for my webpage. And I will be glad to answer your question as much as possible from me, good luck, thank you again for listening to all these lectures.