Introduction to Polymer Science Prof. Dibakar Dhara Department of Chemistry Indian Institute of Technology-Kharagpur

Lecture-42 Polymer Blends, Concluding Remarks

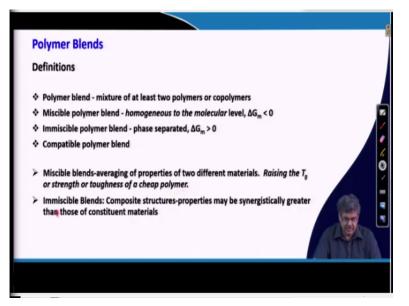
Welcome back, in this lecture and this will be my last lecture for this course.

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

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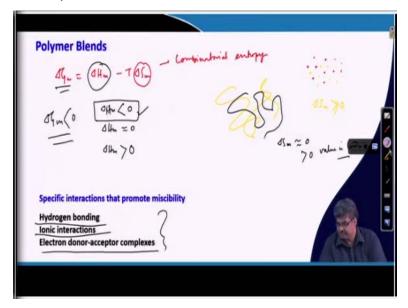


When we discuss polymer blends, it means a mixture of two or more polymers, which could be homopolymers as well as copolymers. When these polymers are mixed in a homogeneously at molecular level, we call this as miscible polymer blend and that happens when the Gibbs free energy of mixing is less than zero or negative $\Delta G_m < 0$.

When this Gibbs free energy of mixing is positive ($\Delta G_m > 0$) then this polymer blend actually forms an immiscible polymer blend where the different polymers form different separated phases. Sometimes these immiscible polymer blends which are actually present in different phases, they can be kind of tied to each other so that they do not get separated further by using some compatibilizer and which creates compatibilized polymer blends.

Miscible blends have an average of properties between two polymers, for examples, if we are using two different polymers having two different T_{gs} , then it will raise the T_g of the lower component, or it will raise the strength or toughness of a commodity polymer. Sometimes miscible blends are created to increase the strength or T_g or the toughness of a commodity polymer by adding some other polymer.

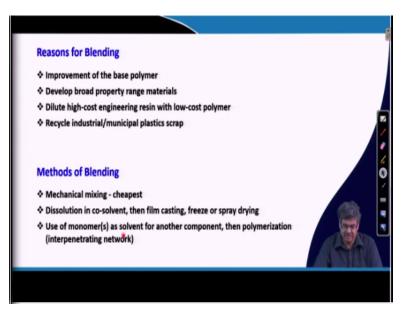
Immiscible blends have a composite structure and properties are synergistically greater than those of constituent materials. Sometimes deliberately immiscible blends or compatibilized blends are created so that the property or the performance of the blend is better than individual constituents.



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When we talk about thermodynamics of polymer blend, if we talk about $\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix}$. Now for a given temperature and pressure as we discussed in our lectures on polymer solution, a combinatorial entropy comes because of the change in conformation of the polymer molecules. Now when you mix two different small molecules, say molecules of different color, invariably the entropy of mixing is positive, because there are many combinations possible. When we mix small molecules, invariably ΔS_{mix} is much higher than zero. 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, say if you mix two different polymers, as the polymers are large in size, the value of this combinatorial entropy of mixing is low, either very close to 0 or they are positive but the value is very low. So, the polymer - polymer miscibility is mainly determined by the value of ΔH . If ΔH_{mix} is negative then miscibility is favorable, if ΔH_m is close to 0 then it is either miscible or immiscible depending upon the value of ΔS_m which depends on the molecular weight as well. The higher is the molecular weight, the miscibility comes down because the value of ΔS_m becomes close to zero. Lower molecules are probably better miscible; if we have ΔG_m positive, then obviously they are not miscible. Therefore, to have two polymers becoming miscible with each other, we should have ΔH_m less than zero and that happens if there are strong inter-polymer interactions, attractive interactions between these two polymer chains. That happens if we have say hydrogen bonding between polymer chains, ionic interactions or electron donor-acceptor complex formation between polymer chains. If these things happen then there is strong attractive interaction between polymer chains and that helps the value of ΔH to become negative. As a result, ΔG becomes negative and the polymers become miscible with each other.

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Now why should we blend? Because it improves the base polymer, especially if the base polymer is a commodity polymer. Then we can add some other polymers to improve the performance of the base polymer. It actually helps in developing broad range of properties. Any two polymers we can mix in different ratios to make different grades and basically have different products. Obviously if we use two polymers with different costs, the blend cost will also vary but if the final application does not require very high property, then we can use probably a cheaper polymer, and blend with the higher polymer component and use that. So, we can actually use the blends to

develop a range of material, dilute the cost of engineering resin with low cost polymer, and it can help in recycling the plastic waste.

The methods of blending 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 film or by freeze drying or spray drying, but this is a very costly affair. Especially the use of solvent is also hazardous. We can use kind of polymerization technique where a polymer solution can be used as a medium to polymerize another monomer. So the second polymer is formed in presence of the first polymer to give a kind of interpenetrating network, but it is not a blending process because we are not mixing the two polymers.

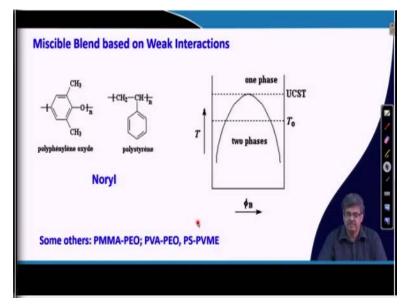
Polymer Blends

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This is a possible phase diagram. Not necessarily each polymer pair will have a LCST at different regions. This is the total possible scenario, which is captured in this phase diagram. The value corresponding to lower critical solution temperatures means that below this temperature the two polymers become miscible and above this temperature depending upon the composition, it can remain either in miscible or in immiscible phase.

And within this immiscible phase, we can have a metastable region and a completely phase separated region. Similarly, we can have another scenario where above a certain temperature, the

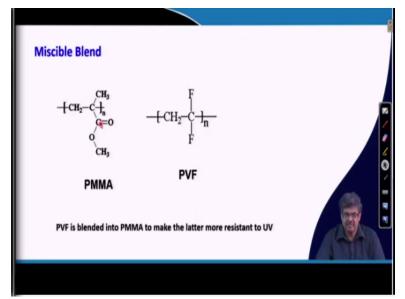
polymers become miscible, they have a single phase and the particular temperature is called upper critical solution temperature or UCST below which depending upon the composition either we can have a single phase or a two phase scenario.



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Some examples of miscible blend with weak interactions like blend of polyphenylene oxide and polystyrene. The other examples are like PMMA-PEO, PVA-PEO PS-PVME, are miscible blends having weak interactions.

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Other examples of miscible blend are like PMMA and PVF. In this case PVF, which is a costlier polymer, is blended into PMMA to make UV resistant PMMA.

T, for Blends Miscible: single T Immiscible: Two T, Partially miscible: $=T_{*}^{1}$ and T_{*}^{2}

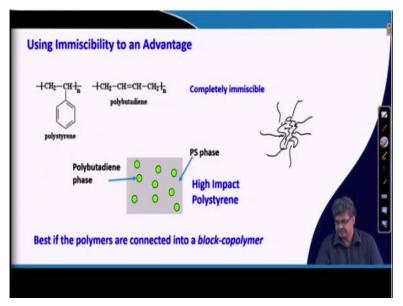
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For a blend, the T_g is given by the miscibility properties of the blend components. If they are miscible, there is an average single T_g which is given by this expression. This is the most accurate equation which can be used and this is Fox equation, as I have mentioned earlier where these T_g^A and T_g^B are the T_g s for polymer A and polymer B respectively.

$$T_g^{blend} = T_g^A w_A + T_g^B w_B$$
$$\frac{1}{T_g^{blend}} = \frac{w_A}{T_g^A} + \frac{w_B}{T_g^B}$$

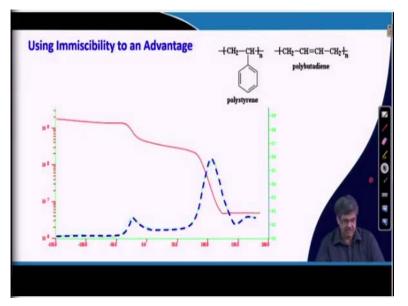
If they are immiscible then we get two T_g s for the individual homopolymers and if they are partially miscible we still get two T_g s but the T_g s in this blend are different as discussed earlier.

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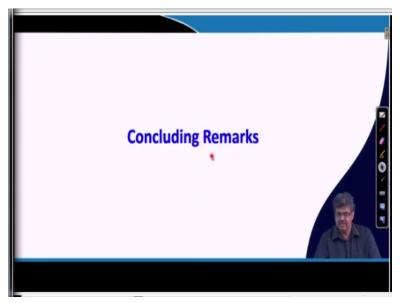
Now we can use this immiscibility to our advantages, for example polystyrene is a brittle polymer. So to improve the impact behavior or ductility of polystyrene, polybutadiene rubber is added. Now if they were completely miscible then we would form a single phase and the impact property of polystyrene would increase marginally because of presence of polybutadiene. However since they are immiscible, we can have polybutadiene added to the polystyrene matrix. As a result, this polybutadiene will phase separate and remain as this type of phase separated material. We can use some compatibilizers to compatibilize these blends or we can have covalent bonding between this phase with polystyrene matrix. As a result, this polybutadiene phase will act as an impact modifier. As a result, this blend of polystyrene and polybutadiene is an example of high impact polystyrene. It is best if we have polystyrene connected covalently with polybutadiene as a block copolymer. That is generally done by making polybutadiene core containing residual double bonds, and from that core, polystyrene is generated to make a core-shell type polymers that will have high impact.

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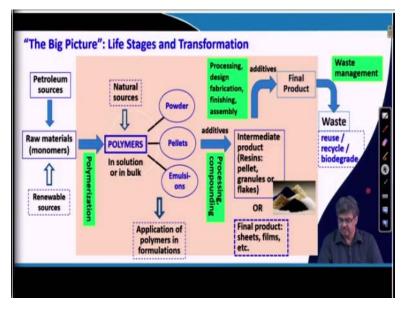
If we do a DMA of this polystyrene-polybutadiene sample, we can see a T_g corresponding to the polybutadiene phase and a T_g corresponding to polystyrene phase and this is tan δ . Therefore, you can see there is a maximum here corresponds to the T_g of polybutadiene, and there is a maxima around 100 ° C which corresponds to the T_g of polystyrene molecule. A plot of G, G' and tan δ is shown in the slide which gives the value of T_g of PS and T_g of PB. We now see that there is always a good reason why we want to make either miscible blend or an immiscible blend. It is not that always it is better to prepare a miscible blend, sometimes immiscible blend like the example shown here also improved the property of the base polymer.

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

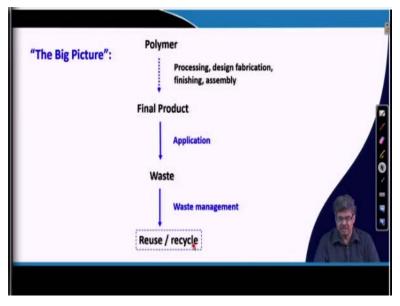
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If we go back and remember this slide, this is the complete picture of life stages and transformations, starting from the source of the polymer, monomers and polymer, and then polymerization and then product. The only part we have not discussed is about the source of the raw material and the waste management. In fact, these are 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 reducing day by day because of evolution of electric cars and electric vehicles. As the demand of oil is slowing in that aspect, so the concern of supply of monomers from those crude is actually coming down. Therefore, this part is probably is not that concerning now. Rather, it is more important to think about what to do with these polymer materials and most of the issues with polymer materials are because of an improper or bad management of the polymer wastes.





If we go back and look again, polymers actually give you the final product using these steps and then, after the application, the wastes are generated which is very vital i.e. how we manage the resulting waste. We should be either reusing this material or we should be recycling, that is most important.

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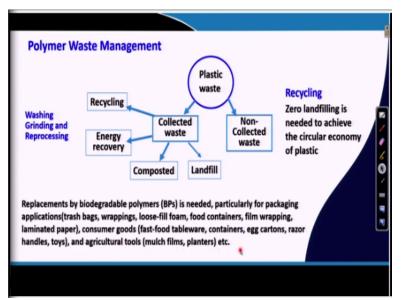


So, if we look at the polymer waste management, the most problematic aspect comes when use long lasting polymers for short lived applications like packaging, carry bags and bottles. This is a short lasting application as we drink water from bottle and throw it. Basically, the application duration is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

Most of the today's synthetic polymers are produced from petrochemicals and are not biodegradable. So, these polymers are a significant source of environmental pollution and they harm wildlife when they are dispersed in nature like in seawater. We always see pictures 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.

Plastics after use are often soiled by food and other biological substances and so making physical recycling of these materials are kind of impractical and generally undesirable. If we use a bottle for storing a juice or some other things, and then these bottles or these packets actually get contaminated with food or other substances which came in contact with this material, as a result physical recycling is very difficult.

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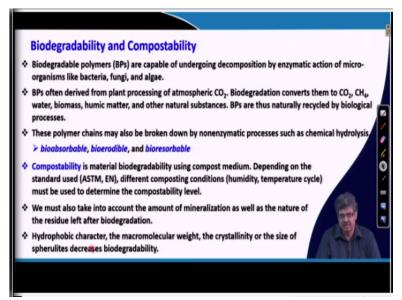


So, what generally is done with the waste? There are mainly two types of waste, the collected waste and non-collected waste, the major one being the collected waste that is collected from waste bins and then either recycled or incinerated and used as an energy source. Alternatively, they can be made into compost using microbes to further use as a monomer resource back to polymer industry or as a fertilizer. 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 actual problems come from the non-collected wastes like those plastics, carry bags or bottles which are thrown away in places where these are not collected. So, if we can reduce this non-collected waste and that can be only done if all of us who are using plastics, can actually dispose the plastics in proper way so that when these plastics waste can be collected and either of the above four processes can be applied to them 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 polymers. Then even if we do not collect this material properly, it will not do as much as harm as the non- biodegradable polymers.

Now after collecting the polymer waste, for recycling or other processes to happen, with these, collected waste need to be washed. If they are used for recycling then it has to be grinded and reprocessed for making further product, which is also not cost effective. As a result, there is always an economic challenge in polymer recycling unless we can reuse and find a high cost application.

Since these polymers are not base polymers, they are not 100% pure. As I discussed, they have additives, fillers and as a result, they cannot be used for the original applications, like if one plastic or polymer was used for a water bottle then that cannot be recycled back again for making a water bottle because of presence of additives and other contaminants.

Hence, these recycled plastics are generally used for low end applications, non-food or non-health related applications. Generally, when you see a black polymer like this black bin or dustbin bags, these are generally synthesized from recycled plastics. So, zero landfilling is needed to achieve circular economy of plastics. Therefore, whatever plastics we can collect from waste, if we can recycle all of those back to the system with zero landfill and zero non-collected waste, then we can have a circular economy for plastics. So, replacements by biodegradable polymers are 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 or microorganisms like bacteria, fungi and algae. These biodegradable polymers often are derived from plant processing

of atmospheric CO_2 . So, plants actually process as basically they collect the CO_2 and from which the biodegradable polymers are actually synthesized.

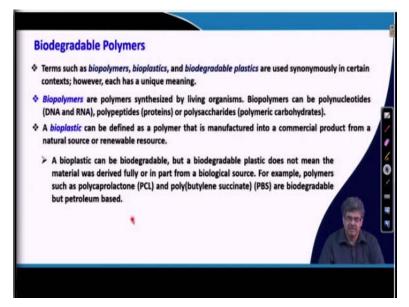
Biodegradation is the process, which converts back these biodegradable polymers to carbon dioxide, CH₄, water, biomass, humic matter and other natural substances. Thus, biodegradable polymers are naturally recycled by biological processes. These polymer chains may also be broken down by non-enzymatic processes such as chemical hydrolysis but these are not very commonly encountered by normal plastics.

Because if they anyway get hydrolyzed in presence of some chemicals or some non-enzymatic processes, then their usefulness also will come down, because during use also it will hydrolysis and the property degrades. Sometimes these biodegradable terms are replaced with bioabsorbable or bioerodible or bioresorbable materials, they all mean same.

Compostability is 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 some standard conditions to be applied which is given by the regulatory agencies.

We also must take care about the amount of mineralization happening and the nature of the 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. As you know, during compostability, water is a factor. If the polymers do not come in contact with water, then obviously compostability or degradability becomes lower and lower.

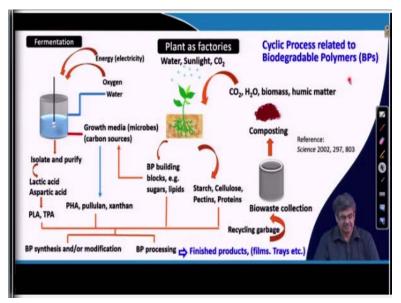
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Sometimes these terms like biopolymers, bioplastics, biodegradable plastics are used synonymously in certain contexts but each has unique meaning. For example, biopolymers are the polymers synthesized by living organisms. They can be polynucleotides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

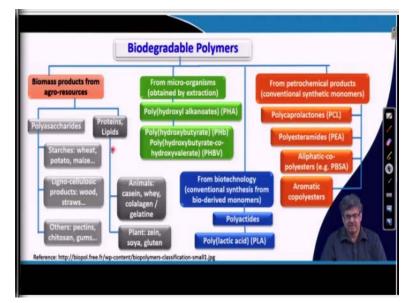
So, there is a little difference between biopolymers and bioplastics. A bioplastic can be biodegradable but a biodegradable plastic does not mean the material was derived fully or in part from biological sources. For example, polymers such as polycaprolactone or polybutylene succinate, they are partially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

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A cyclic process related to biodegradable polymers is shown in the slide. Plants, with the help of water, sunlight and carbon dioxide, produce raw material for biodegradable polymers. For example, they produce starch, cellulose, pectin, that are biodegradable polymers and are directly used as such for making products. They also make building blocks for making biodegradable polymers like sugars and lipids, which can be polymerized to make biodegradable polymers. They give these sugars and lipids, which can be actually converted using biotechnological route (like using microbes) into 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 monomers for making biodegradable polymers like poly lactic acid or thermal polyaspartate and so on.

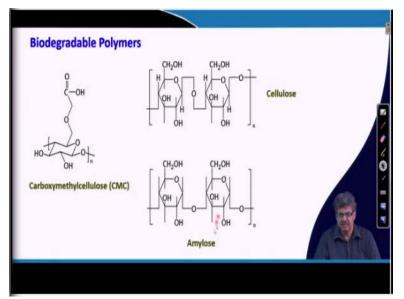
There are four different ways we can synthesize biodegradable polymers but the source has to be from plants. They can directly produce biodegradable polymers or they can produce monomers, which can be converted to biodegradable polymers. They can produce monomers which can be converted to biodegradable polymers using microbes, or they can be converted to other monomers by fermentation process which can be again polymerized to produce biodegradable polymers. Once the polymers are produced, they can be used to make different products and after using those products they can be recycled back. By composting, we can get back this raw material which can be either used as fertilizer or for the agriculture applications. So, this gives you a cyclic picture for biodegradable polymers.



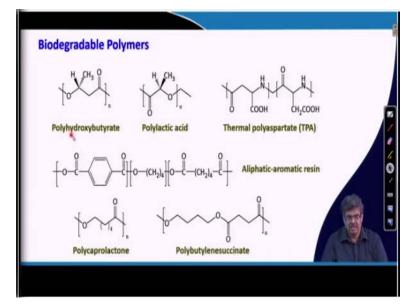
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These are the four types of biodegradable polymers we described and there are names corresponding to them, as given in the chart. In addition to the four biodegradable polymers discussed in the previous slide, there are some synthetic polymers like polycaprolactone, polyester, amides especially aliphatic polyesters that are also either partly or fully 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, and some synthetic polymers like polycaprolactone, poly butylene succinate 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	Existing/Future – Manufacturing Capacity
Reliance Industries	205	445	500	2700	725		970	6545	41.46	Capacity
Indian Oil Corp		225	475	600				2000	12.67	Major Indian
Haldia Petrochemicals		210	500	390				1100	6.97	Players
GAIL (India)		350	570					920	5.83	(Thermoplastics)
HPCL Mittal Energy				440				440	2.79	
VL Dhunseri Petrochem							480	480	3.04	Source : PLASTINDIA
Supreme Petrochem						340		340	2.15	FOUNDATION
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	ALL AND
ONGC Petroadditions Ltd		360	700	340				1400	8.87	ACT THE REAL

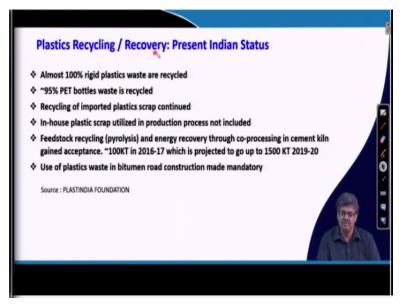
These are the main companies in India which produces plastics e.g. Reliance Industries, Indian Oil Corporation or Haldia Petrochemicals. The products are listed here, and then their amount and the percentage of share also as mentioned in this. So, this is just to give you the companies which basically make polymer in our country.

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Year	GDP Growth (%)	Polymer Consumption Growth (%)	Import Duty	
990-1995	5.0	12.9	50%+	
995-2000	6.5 📢	14.6	40%	
000-2004	5.9	5.8	45%-15%	
005-2012	8.7	10.9	12.5%-5%	Source : PLASTINDIA
012-2017	7.2	10.6	7.5%-5%	FOUNDATION
017-2022	8.0	10.4	5%-0%	

There is a steady growth as our GDP grows steadily with time, the growth of polymers also increasing steadily with 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 wastes are recycled and for example 95% PET bottle wastes are recycled. The regulatory agencies are trying their best and in fact the situation is not that bad at present. Only the single use plastics like those used in packaging materials, causes most of the 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 arise.

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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 the world. Flexible packaging industry poised for strong growth and insulated from current economic scenario due to huge and diversified consumer base and plant 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 slide that as a polymer scientist or a polymer chemist you should not be having any doubt about the future of polymers or plastics. For example, look at the current pandemic situation. All these PPEs, which are being used by doctors and nurses are all made from polymers. We are talking about the medical equipment, medical disposables like syringes and gloves and all these things; they are all made from polymers. So, although polymers have a kind of bad name because of their environmental hazards, but this is responsibility of 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 plastic waste.

With this we come to the end of the course and hope you enjoyed this course on introduction to polymer science. Good luck, thank you again for listening to all these lectures.