Science and Technology of Polymers
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Lecture - 35
Multi Component Polymeric Materials

Good morning, today the topic of our discussion is multi component polymeric materials, when we talk about polymer technology, which is polymer product technology. We think of some products made of merging polymer materials, along with some functional additives. Now, there are certain limitations of that product technology made from individual homo polymers.

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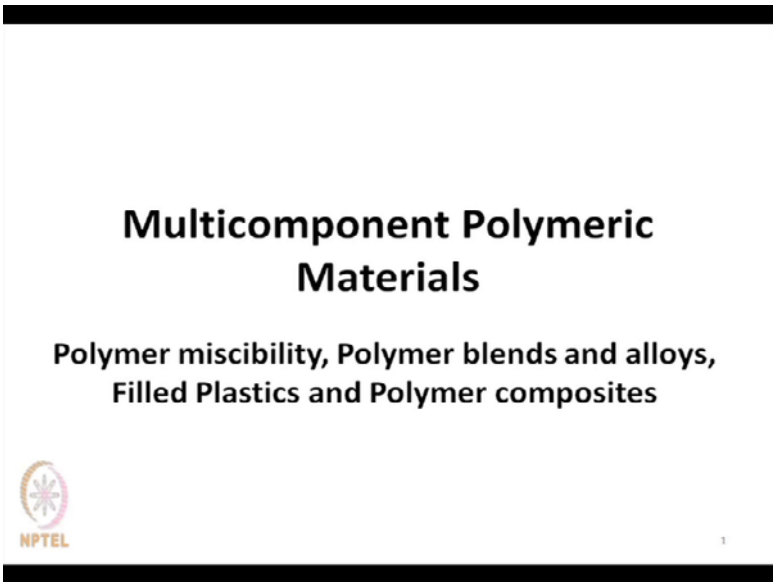

So, there were enough reasons to find out improvement in the properties of the product. For that reason, people have developed some polymer products which are better than the products made from single polymer materials to develop a broad spectrum property in the product.

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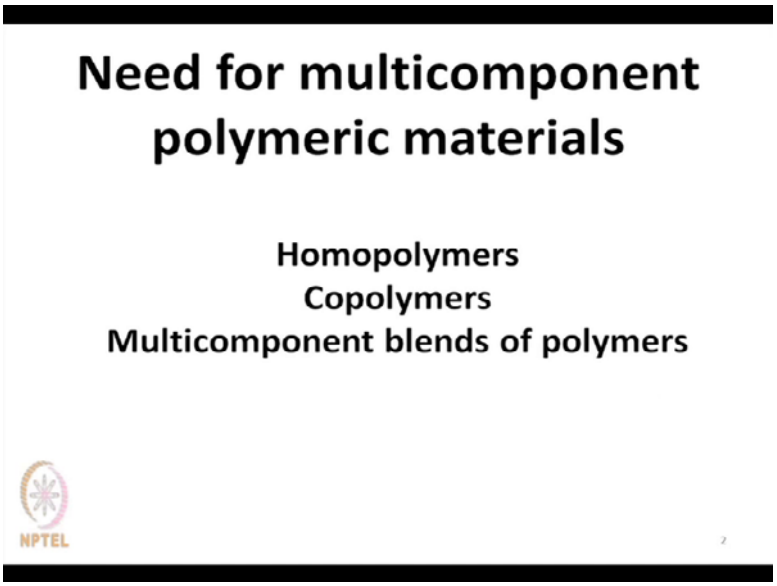

So, basically a need is felt for such type of products, which are supposed to provide broad spectrum properties as well as better properties or improved properties over the properties contributed by a single polymer in the product. To explicitly explain, we know about the homo polymers, we know about the copolymers, the difference between the homo polymers and the copolymers lies in the fact that homo polymers are made from a single monomer.

This means the monomeric unit repeats along the entire backbone of the polymer chain and we get a polymer when the properties of that homo polymer are not sufficient enough to obtain the desirable performance of the product. Then, people thought about mixing a second monomer or a third monomer with the first monomer to form a new product which is known as copolymer. This means polymers made or synthesized between more than one monomer, so that the monomer units of the different monomer units act here along the backbone chain in a different sequence.

I discussed in other lectures that is the monomers, when they are arranged in an alternating sequence or alternation sequence that is called alternating copolymer. When the monomers, monomer units of two different monomer units are arranged in a block sequence, block of one monomer followed by the block of the second monomer. Then, we get block copolymer; or the monomers, two monomers can be arranged in a random fashion along the backbone chain that is called random copolymer.

Not only that, it can be a graphed copolymer that means onto the backbone of one of the homo polymer of the monomer, a second monomer is polymerised, so that it is grown or starts from the backbone of the first polymer. So, the second polymer becomes grafted or becomes attached to the first polymer chain, so that is graphed copolymer.

So, this way these copolymers were developed and as it was expected that such copolymers are supposed to provide better polymer better products properties or improved properties or broad spectrum properties. This is not present in one homo polymer, that was successful that means the properties of the two monomers can be developed in a copolymer.

Similarly, when people could not be further satisfied with this either homo polymer or copolymer, then people thought about of multicomponent blends of polymers that means more than one polymers are mixed together. So, there are lot of science behind this copolymer synthesis, copolymer properties and the science behind the multicomponent blends or the blends of more than one polymer to form a new product, I have discussed to some extent in other lectures.

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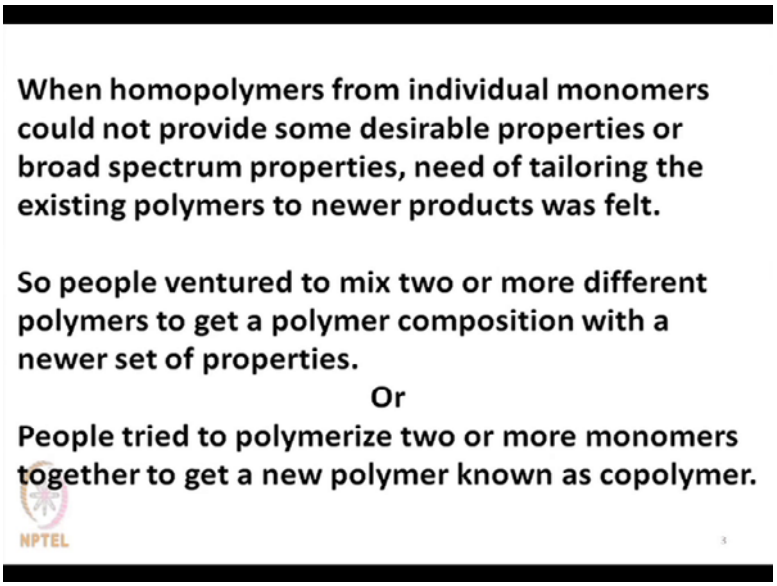

Now, here when homo polymers from individual monomers should not or cannot provide the desirable properties or cannot provide broad spectrum properties need of tailoring the existing polymers to newer products was failed. So, people ventured to mix two more different polymers or to get two more different polymers or to get a polymer composition

with a newer set of properties. People tried to polymerize two or more monomers together with the other monomers to get a new polymer known as copolymer. So, this way the existence of or the development of copolymers and polymer blends were formed.

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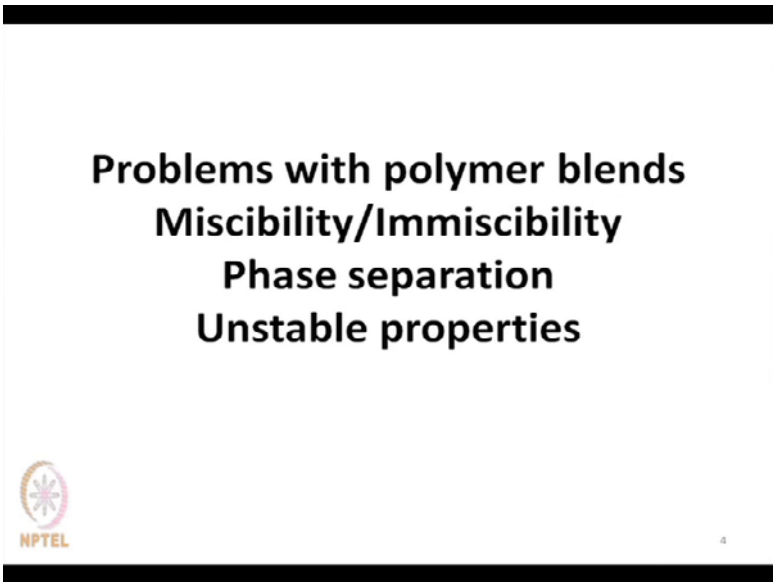

Now, what are the problems or if there are any problems if we go through or if we go for synthesis of copolymers or the polymer blends. In case of copolymers you know that the monomers different monomers are attached to an attached to one another through covalent primary bonds or primary covalent bonds.

So, basically that polymer made from two monomers are not a mixture of two polymers rather different properties of different monomers are introduced in one polymer having the presence of two different monomers in a different sequence. In case of polymer blends that is that is good in case of your copolymer there is a success in developing newer properties there is a success in the developing broad spectrum properties. When people went for mixing more than polymer or two polymers, three polymers like this then a problem was faced, so when polymer 1 is mixed with polymer 2.

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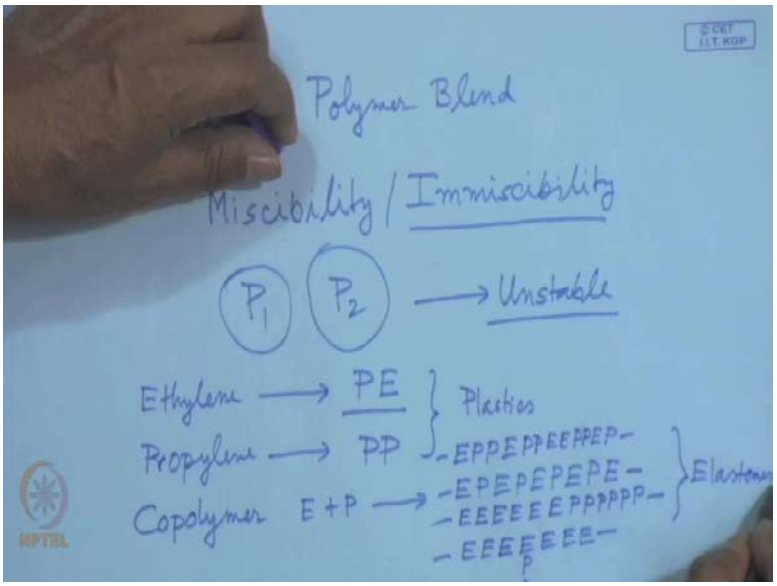

P 1 is mixed with P 2 a product known as polymer blend is produced now there are many considerations to be thought of in this particular issue. Now, what is the nature of polymer 1, what is the nature of polymer 2, how they are mixed, after mixing how they show the properties or what about their phases two different phases of the polymer 1 and polymer 2. All these things are to be considered. In that angle, we have to discuss about the miscibility immiscibility of the component polymers miscibility immiscibility of the component polymers.

If, the component polymers are not miscible, then what will happen? The phase 1 will separate from phase 2, which means there will be separation of different, when it is produced by some process. Initially, we can have improved properties or the combination of properties or the addition of properties of polymer 1 with the polymer 2, but in the long run during service in the during the service of the product during the use of the product. With time there will be separation of polymer 2 phase from the polymer 1 phase, so that leads to unstable or instability in properties. So, that is not a desirable phenomenon the product should maintain its properties for a longer period or even up to its end use end of life.

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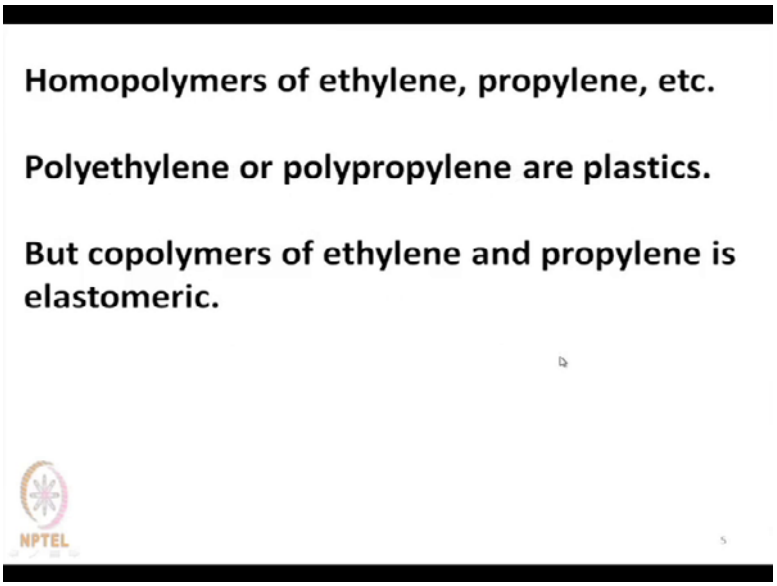

So, miscibility immiscibility phase separation these aspects are to be considered if we discuss with examples. Let us take the examples of homo polymers of ethylene which is polyethylene P E there are different grades LDP, EHD, PEL, LDP, EBL, DPE ultra high molecular rate polyethylene. So, those are all homo polymers, but the different grades differ from each in terms of their micro structure, their molecular weight, their branching non branching density. Similarly, propylene also gives a homo polymer polypropylene same is the situation with polypropylene.

So, these are known as very good plastics, as I mentioned if we want to have a multicomponent polymer that means in one polymer there can be more than one component. I want to have you want to have ethylene component in the polymer along with the propylene component in the polymer, so we can synthesize a co polymer of ethylene and propylene, so it will form a copolymer of EPE, PEP like this.

So, if we plus this ethylene and propylene units in alternation, we call it ethylene propylene co polymer, if we place this ethylene propylene units in the form of blocks ethylene blocks followed by propylene blocks like this, we call it block copolymer. We say it continuous, if we want to graphed ethylene propylene on to the main backbone chain of ethylene. It looks like this from here the propylene segments can grow, this is graphed copolymer.

Similarly, we can have random copolymer ethylene propylene propylene ethylene, this random ethylene units are propylene units are randomly placed in along the back bone chain of the polymer random placement. So, random copolymer, here in doing, so the properties of homo polymers are drastically changed in the co polymer because of the presence of the two monomer units in the backbone chain. This copolymer of ethylene propylene becomes elastomeric in nature, whereas their homo polymers are plastic.

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Some definitions for polymer alloys and blends

Polymer blends (PB)	Mixture of polymers and/or copolymers
Polymer alloys (PA)	PBs with modified interfacial properties and or morphology
Miscible PB	A single-phase PB system with molecular level of dispersion, when $\Delta H_m < 0$
Compatible PB	Homogeneous system with enhanced physical properties
Compatibilization	Any physical/chemical action which stabilizes a PB without phase separation
Engineering polymer (EP)	Processable polymer, exhibiting high mechanical properties at continuous use temp above 100^0C with a TS > 40 MPa
Engineering PB (EPB)	PA or PB containing EP as at least one component of the blend

Before going to discuss about this, little details of this multicomponent polymeric systems, we must look at the definitions of some terminologies, sometimes we hear as polymer alloy.

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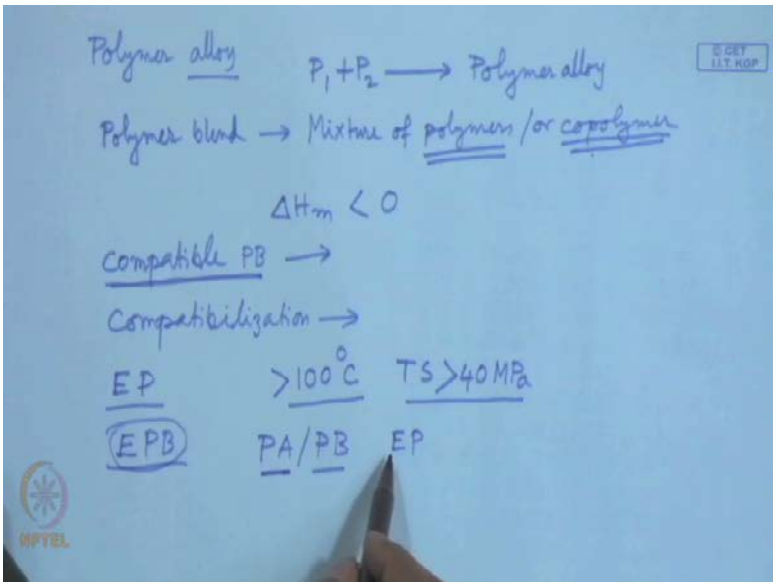

This terminology alloy is used in case of metal alloys metals and alloys means that is a solute solution of one metal in another metal that is solute solution, similar is the case for polymer alloy. So, we can consider that if one polymer becomes soluble in another polymer, that means one of the polymers can act as solute and polymer can act as solvent in that case we can get a polymer alloy. Again, if we take this example of polymer P 1 and polymer P 2, so this product will be a polymer alloy, provided they form a solute solution. There is a molecular mixing and the chance of separation into phases all these things does not occur at all.

So, that is called polymer alloy, then what is polymer blend? Polymer alloy can also be called as polymer blend. Now, this polymer blend is a mixture of polymers mixture of more than one polymer with other polymer or mixture of a polymer or a co polymer and or mixture of two co polymers. So, polymer, polymer mixture, polymer polymer mixture, co polymer, co polymer mixture or polymer, co polymer mixture. So, these different cases, different blends of polymer, polymer, co polymer co polymer, co polymer are formed constitutes this polymer blends.

Then, what is miscible P B, miscible poly blend? It is a single phase poly blend system is supposed to be a single phase poly blend system at molecular level of dispersion of one polymer in other. It must fulfil the thermodynamic criteria that are heat of mixing of the two polymers should be negative, when delta H of m that means heat of mixing of the

two polymer is negative. Then, other terminology also we come across that is compatible poly blend when the two polymer components mixes mix it get a polymer blend. There, the question of this two components miscibility or the compatibility phase mixing of the two component polymers or interfacial addition of one polymer molecule with other polymer molecule that is known as compatibility.

So, that leads to compatible poly blend and it can be considered as a homogeneous system with enhanced physical properties, which is intimately mixed, molecularly mixed to form a homogeneous solution homogeneous mixture. We can consider that also as polymer alloys there is nothing wrong in it and by doing, so we can have improved or enhanced physical properties of the as well as the chemical properties of the polymer blend.

Then, we want to make this compatible poly blend, then what is the main sub compatibilization, what is the meaning of this term compatibilization? Now, any physical or chemical action which stabilizes a poly blend without phase separation is known as compatibilization. This means, a polymer B to be blended with polymer A to make it compatible for that action there must be some chemical or physical interaction between the two component polymers. That physical or chemical action must stabilize the system of the poly blend without any chance of phase separation. Now, there is another terminology is engineering polymer E P engineering polymer.

Now, engineering polymer is also considered as a processable polymer, which is supposed to exhibit high performance properties say high mechanical properties at certain temperature where the product is to be continuously used. The product is to perform continuously preferably at a temperature of higher than 100 degree celsius, we say tensile strength of greater than say 40 mega Pascal. So, a polymer which can stand higher than 100 degree Celsius for a prolonged service period maintaining a tensile strength tensile properties of polymer beyond 40 mega Pascal, then the terminology engineering poly blend engineering poly blend EPB.

So, to make engineering poly blend we can take a polymer alloy or a polymer blend in which one of the components should be an engineering polymer that is known as engineering polymer blend. So, a polymer blend once again I repeat a polymer blend

having components P A polymer alloy or polymer blend, either of this two any of these two should be an engineering polymer that is known as engineering polymer blend.

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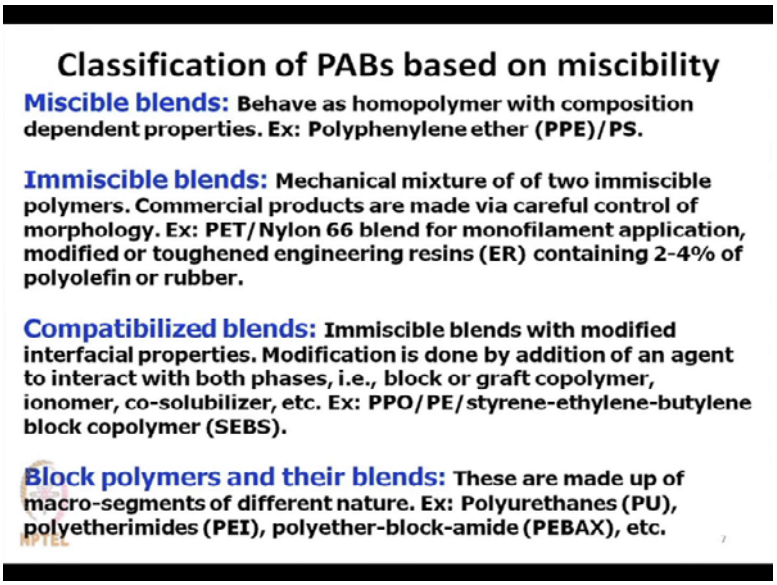

If we look into the classification of this polymer alloys and blends based on their miscibility or their degree of miscibility, degree of mixing, degree of compatibility etcetera the miscible blends should behave as homo polymer.

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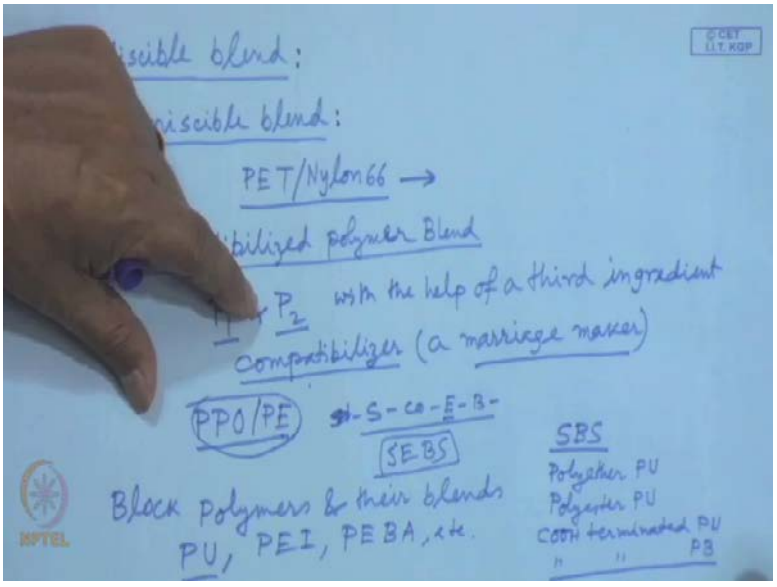

One of the classes of this polymer blends and alloys this miscible blend should behave like a homo polymer that means it can be considered as a substitute of homo polymer. At

the same time, having higher level of properties over those of homo polymers as well as development of newer properties which is not available in the homo polymer and their properties are composition dependent. That means the properties of the blend is dependent on the composition of the component polymers that means either the property available is dependent on 70, 30 basis. This means one component is 70 parts by weight or parts by volume and the other component might be 30 parts by volume or parts by weight.

Now, if we move from 70, 30 to 80, 20 or 90, 10 or 60, 40 the properties of the blend may vary, in fact it happens. So, in order to optimize that one should make blends in wide range of compositions to arrive at the maximum property available from a suitable composition it might be 60 40 or 70 30 or 50 50 that is to be explored.

Next class is immiscible blend, now this immiscible blend is a mechanical mixture of two immiscible polymers here, you must understand that the two component polymers are not miscible. We are blending it, mixing it and the product formed is known as immiscible blend.

So, mechanical mixture of two immiscible polymers and commercial products are made via careful control of morphology for example, polyethylene terephthalate polyethylene terephthalate nylon 6 6 blend for that is used for monofilament application. Now, this polyethylene terephthalate and nylon 6 6 are not completely miscible there are certain immiscibility effect of this two polymers because this two polymers are chemically different. Then, since this two polymers are little polar in nature through polar interaction they can be used for making a blend, but their properties can also be modified or toughened with engineering resins containing 2 to 4 percent of polyolefin or rubber.

So, these polymers can be blended, compatibilized with a mixture of small percentage of some other polymer that can be polyolefin say polyethylene or polypropylene or a rubber. Next class is compatibilized polymer blend, when two component polymers are not compatible in a mixture in a blend well we can also use those component polymers P 1 and P 2 to form a blend with the help of a third material ingredient. That is known as a compatibilizer, we can consider or we can designate this compatibilizer as a marriage maker.

Let this P 1 and P 2 does not like to mix with each other, but since because of the difference in their solubility parameter, their polarities and their other aspects molecular weights, density. So, these two basically immiscible components can be made miscible if a third component third person is brought in between them which is known as a marriage maker, that marriage maker is known as compatibilizer. So, with the help of the compatibilizer two immiscible polymers can be converted to a polymer blend.

Now, this modification is done such modification with the help of compatibilizer is done by addition of an agent which is known as compatibilizer, this compatibilizer interact with both the phases. So, this can be a block or graft copolymer, this can be an ionomer, this can be a co solubilizer means a co solvent type of thing. This means, the third component which is used as compatibilizer can interact with the both.

So, they can keep both the polymer components P 1 and P 2 miscible by the presence of this third component, examples are poly phenylene oxide P P O and polyethylene. These two and these two are compatibilized polyethylene is purely hydrocarbon, polyphenylene oxide has got some polar nature.

So, that is compatibilized with the help of styrene ethylene styrene co ethylene co butylene copolymer. So, because of the presence of this phenylene of styrene, presence of ethylene unit, presence of butylene units. So, these help to make this two component polymers miscible, so this is known as SEBS. So, S E B S can be used as a compatibilizer can act as a compatibilizer, then comes this block copolymers, block polymers and their blends this block co polymers. Their blends these are made basically made up of macro segments of different nature say polyurethane, poly etheramide, poly etherblockamide, polyetherblockamide etcetera.

So, these polymers have macro segments means segments are the molecular weight of that segment is higher than that of a monomer unit. So, that is why they are known as macro segments, so that is known as block polymers and their blends say styrene block styrene, butylene block copolymer SBS also SBS.

Similarly, polyether polyurethane, polyester polyurethane, similarly carboxyl terminated polyurethane, carboxyl terminated poly butylene there may can be many examples to be cited in favour of that block polymers and their blends. So, there are so many block polymers they can be also blended to form a new product having newer set of properties.

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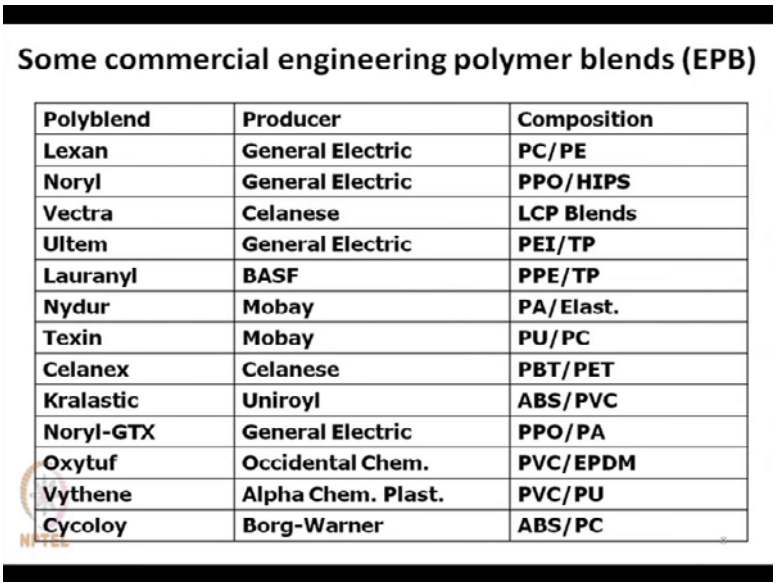

Let us look into some commercially available polymer blends or commercial blends, there are plenty of examples, you can get details of those examples in other literature just to mention examples of few. Lexan is the trade name producer is manufacturing General Electric Company and the component polymers in that blend is poly carbonate and poly ethylene. It is fantastic poly carbonate is a polar polymer, it is an engineering polymer, poly ethylene is a non polar polymer, it need to be hydro carbon polymer. Now, the purpose behind the blending of these two polymers is that this polarity of this poly carbonate is altered by the presence of polyethylene or the hydro carbon nature non polarised nature is altered by the presence of poly carbonate.

So, by varying the composition of poly carbonate and poly ethylene, we can have some new properties in some particular composition. So, this blend is available in the market, similarly Noryl is polyphenylene oxide and high impact polystyrene blend mixture of high impact polystyrene with poly phenylene oxide Vectra, produced by Celanese corporation. Basically, a liquid crystalline polymer blend more than one liquid crystal polymers are mixed to develop a composition which is better properties than individual liquid crystalline polymers.

Again, manufactured by General Electric it is a poly etherimide blend with thermo plastic polymer poly etherimide is blend with T P thermo plastic polymer. Lauranyl made by B A S F germany polyphenylene oxide polyphenylene ether with thermo plastic

polymer, Nydur is polyamide with an elastomer. Texin Mobay is the manufacturer polyurethane polycarbonate blend. Then, Celanex made by Celanese Corporation it is a blend of poly butylene terephthalate with polyethylene terephthalate.

Kralastic made by Uniroyl company it is a blend of butadiene styrene tar polymer and P V C poly vinyl chloride. So, there are plenty of examples where the commercial products are available from the blends of different polymers say with polyolefin and with some other condensation polymers, so these are the few examples only.

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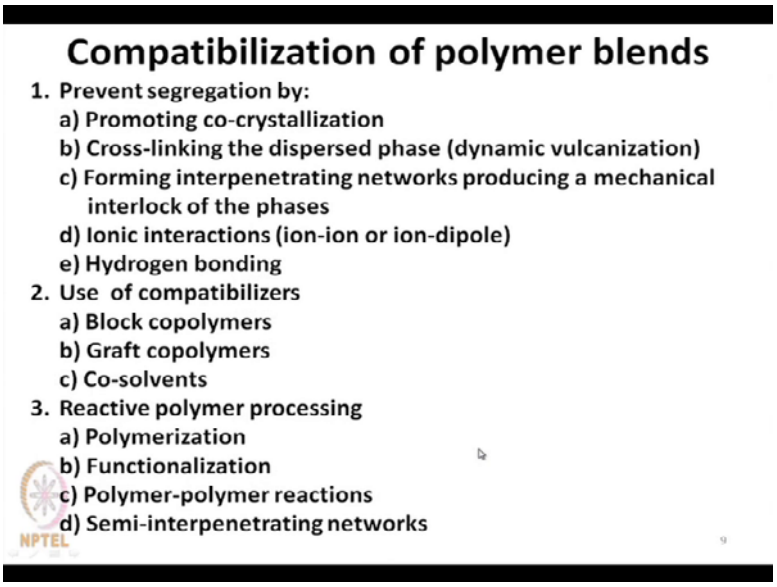

Now, to talk about the compatibilization techniques or the principles of the compatibilization of the polymer blends. This is done to prevent segregation of the component polymers in the blend by promoting co-crystallization between the component polymers. This means this polymers when they are processed by melt processing technique, means they are mixed, then they are fabricated either by injection moulding or by compression moulding or by transfer moulding.

Then, after filling the mould the filled polymer filled mould is cooled the rate of at a specified rate of cooling now that specified rate of cooling, affects this molecular alignment or organizes this molecules to have this long range order in the product. So, either to develop crystallinity or either to crystallize or to not crystallize or to remain or to keep it in amorphous condition. That depends on the requirement if it is required that the products are to be or the polymer molecules are to be crystallized in the product.

This means molecularly aligned to develop long range order molecular order then the cooling rate is properly adjusted so that polymer molecules crystallizes. So, that is a phenomenon of a crystallization during cooling of the product within the mould. Now, that principle has been used as a method of preventing segregation of the component polymers in the blend by promoting co crystallization. Now, the crystallization phenomenon is a kind of purification we know, kind of purification technique means that one material can be purified by crystallizing in presence of other impurities.

So, after crystallization these impurities are removed. Now, here in this case one polymer is supposed to be crystallized in presence of the other that means the nature of the two polymers are chemical nature structure etcetera are almost comparable or identical. Then, two segments of the two polymers different polymer molecules can crystallized together, that means from a crystallite in which one can find the presence of the two different component polymers, that is known as co crystallization.

So, such co crystallization can help to prevent segregation of the component polymers in the blend. This is a kind of this is a one of the principles of compatibilization, second is the cross linking of the dispersed phase..

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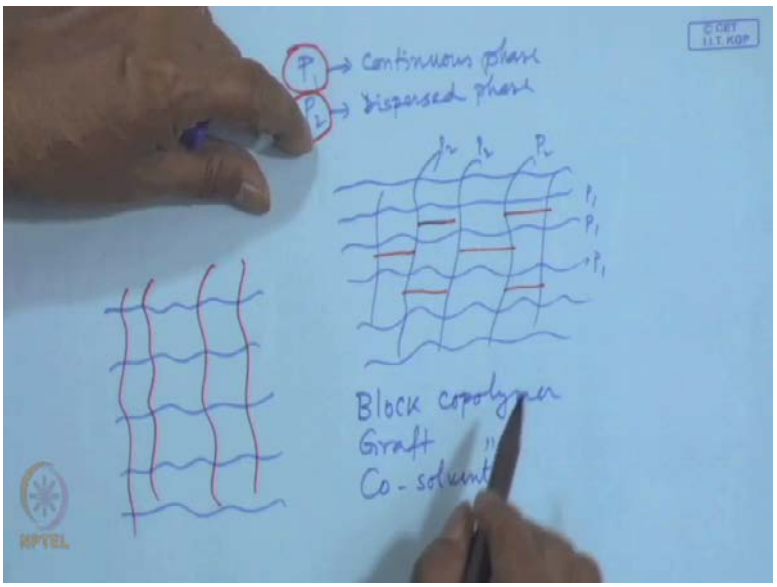

We want to make a blend of polymer 1 with polymer 2, so if we consider that polymer 1 is the major phase suppose it is 70 parts by weight polymer component one polymer with which we want to mix component polymer two having 30 parts by weight. So, this P 2

since it is used with lower concentration this P 2 will remain dispersed in the phase of P 1, in this case P 1 will behave as the matrix at the continuous phase and P 1 P 2 as dispersed phase.

Now, this dispersed phase can be cross linked means this is the phase of P 1 molecules in which is this P 2 molecules are dispersed lower concentration than the P 1. So, these are P 1 molecules, P 1 molecules these are P 2 molecules, P 2 molecules, P 2 molecules.

Now, if this these are intimately mixed P 2 molecules are intimately mixed in P 1 phase that means P 2 is dispersed in P 1 phase in this P 2 molecules are inter linked, if this P 2 molecules are inter linked, only P 2 molecules are inter linked, so what will happen? These P 2 P 1 molecule will remain in the cross linked phase of the P 2 molecule, so that is the kind of compatibilization. That means if P 1 wants to go out of this P 2 P 1 molecules likes to go beyond this P 2 go from the P 2 side, then that will prevent it since there is a network formed by P 2 and this P 1 is entangled with this P 2 network.

So, P 1 cannot move from P 2 separate in to a different phase, so that can prevent phase separation or segregation. So, this is a kind of compatibilization technique by cross linking, then forming inter penetrating network. So, this formation of inter penetrating network is again an extension or modification of this cross linking of the dispersed phase in the phase of P 1 continuous phase. So, this inter penetrating network means we can have a polymer I will discuss later I P N we can have a network of one polymer system in which we can grow another network by polymerising a second monomer in this.

So, it will form a inter penetrating network like this. So, that is also another way of compatibilization in the two components then ionic interactions say polar interactions, say one polymer can have some ionic group, say P 1 can have some ionic group. Now, the ionic groups of P 1 can be interacted with some other ionic groups some other ionic group of P 2 that means the ionic groups of this P 1 and P 2 are not identical. They are different, but since they are ionic say positive or negative ions say positive ions of P 1 can interact with the negative ions of P 2. So, that is called ion, ion or ion dipole interactions that can also stabilize the two different phases in a blend of two component polymers.

Next is hydrogen bonding, it is a secondary interaction hydrogen bonding is a secondary interaction through secondary interaction hydrogen bonding one can stabilize the

segregation or prevent the segregation of the component polymers. That means hydrogen present in one polymer linked to some more electro negative atom and hydrogen present in another polymer link to some electro negative atom. So, these there will be competition of hydrogen bonds between the electro negative atoms present in one polymer with the other present in the different other polymer.

Then, the second principle is use of compatibilizer, as I mentioned earlier that compatibilizers can be of different nature this compatibilizer can be block copolymer or graft copolymer or co solvents. I shall discuss little elaborately later. Then, compatibilization through reactive polymer processing reactive polymer processing, one polymer can be one of the component polymer.

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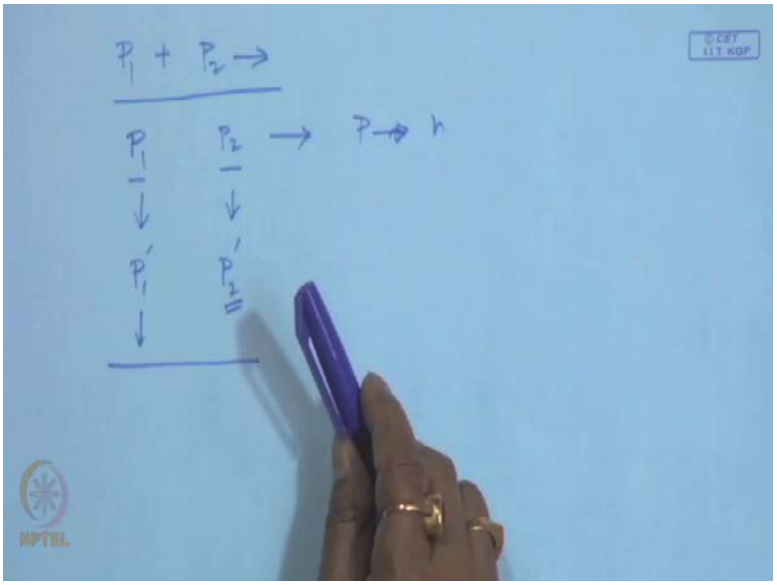

Suppose, it is P 1 it can contain some functional groups functional sides again polymer component polymer P 2 also contains some other kind of functional groups. So, these two function different function groups can in different functional groups present in P 1 and P 2 they can react with each other to form a new product. Through such reaction, this separation of phase P 1 from the phase two or separation of phase P 2 from the P 1 can be prevented or even monomer of P P 2 can be polymerised in the matrix of P 1. That is the technique known as polymerisation through polymerisation, we can also go for compatibilization which is known as one of the techniques of reactive polymer processing functionalization.

One can functionalize, say component polymer P 1 and P 2 these two polymers are available in the market. I want to develop a new product P having different properties from that of either P 1 or P 2. So, I can chemically modify this P to P prime, sorry I can chemically modify this P 1 to P 1 prime.

Similarly, I can also chemically modify this P 2 to P 2 prime that is, done through functionalization of P 1 and P 2 that means chemical modification of P 1 and P 2. For example, we can say halogenate polymer P 1 that means halogen atoms can be added to polymer P 1 so that it becomes P 1 prime halogenated polymer. We can also we may or may not modify this P, suppose if it is a halogenated polymer, then we can mix this P 1 prime with P 2 P 2 is a halogenated polymer.

We can mix this P 1 prime with P 2 through halogenation of this polymer P 1, so P 2 contains halogen atom P 1 does not contain halogen atom. So, we can add or attach some halogen atom so that we can blend this P 1 and P 2, not only that we can attach some other functional groups say we can carboxylate or we can develop hydroxyl groups or even we can develop some free radicals. In either of these two polymers, we can then make a blend of these two polymers P 1 and P 2 and which will be stable in properties then polymer polymer reactions.

Now, polymer 1 as I mentioned earlier this polymer 1 can have some functional groups and polymer 2 P 2 can have another functional groups of opposite nature. So, if they are opposite nature then this two functional groups functional group of P 2 can react with P 1 and this two polymers can interact with each other. The new product the product will be new material having different properties then semi inter penetrating network. This is also another technique by which we can develop new properties in this or we can compatibilize these two polymers.

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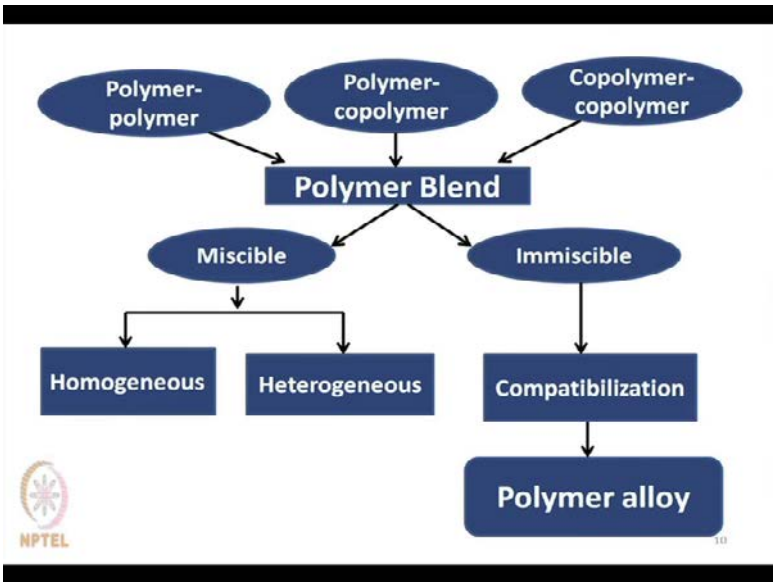

Again, you can view this polymer blend in different way, we can have polymer, polymer blend that means homo polymer, homo polymer blend, we can have a blend of polymer and copolymer, and we can have a blend of copolymer and copolymer. Now, these polymer blends, different types of polymer blends, in which the component polymers can be either miscible or the component polymers can be immiscible. If these component polymers are miscible, then that can again be homogeneous or can also be heterogeneous.

So, depending on our requirement we can make homogeneous miscible blends as well as heterogeneous miscible blends, then if the component polymers are immiscible. Then, we have to take certain measure adaption to do something on the component polymer so that the two component polymers can be miscible that is done through compatibilization. Ultimately, we get a polymer alloy or solid solution of two different component polymers, this way we can get multicomponent polymer system from two different component polymers polar nonpolar they can lead to miscible polymer blends.

Now, a blend of a polar polymer with a nonpolar polymer can be miscible we can make it miscible through compatibilization. Similarly, we can mix a nonpolar polymer in a polar matrix through compatibilization this way we get polymer alloys or polymer blends or polymer mixtures. So, in next lecture we shall discuss the other aspects of these multicomponent polymer systems. Thank you.