Science and Technology of Polymers Prof. Basudam Adhikari Materials Science Centre Indian Institute of Technology, Kharagpur Lecture - 37 Multicomponent Polymeric Materials (Contd.)

We are discussing on the effects of concentration of component polymers in the blend, on the on there properties.

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So, we are talking about additive behaviour, synergistic behaviour and in compatible behaviour and in compatible behavior due to incompatibility of the blends.

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This can be viewed in other ways if you look at the diagram, so 4 different cases, one case is miscible, second case is semi compatible, third case is incompatible and fourth case is synergistic. The previous figure which is showed in the previous figure broken into four different cards, so these completely explains the effect of concentration of polymer component in a on the properties of the polymer blends. In case of complete miscibility properties are more or less proportional to the contents of the two polymer components in the blend, here you see this proper this pro pro properties are proportion to the property of proportion to the properties of the components in the blend.

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Here, the commodity polymers can be the kind of features found in the case of commodity polymers, which has blended in different proportions to meet the specific requirements of each product to be manufactured.

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The example of such additive effect of miscible components are say Noryl, Noryl is a mixture of polystyrene which is a commodity polymer has well it is a cheap polymer, which is

polystyrene cheap polystyrene polymer poly phenylene oxide which is relatively expensive polymer, this two are blended. Now, poly phenylene oxide is a (()) polymer has well it contains aromatic ring in the back bone chain, phenylene on the back bone chain.

And polystyrene is a purely hydrocarbon polymer in which the backbone chain is made of carbon, and phenylene is present has pendant group has substituent of one of the hydrogen's of alternate carbon atoms. It has been found that the properties of noryl are additive of the properties of component polymer of polystyrene and phenylene oxide PPO. Noryl has poorer thermal stability than the either the phenylene oxide poly polymer, but it is easier to process it shows poly phenylene oxide is a thermal stable polymer, polystyrene is thermal stability is lower than that of poly phenylene oxide.

In order to increase the process ability this polystyrene is blended with poly phenylene oxide with compromise of thermal stability of poly phenylene oxide, but possibility was in proved. So, not only the internal performance property, but the processing property is also important, if the polymer although having the high performance properties like with high mechanical strength, high thermal stability etcetera, etcetera. If that polymer could not be processed, that is of no use so in order to make it process able or in order to reduce, it viscosity during processing at lower temperature.

So, such type of component like polystyrene and have blended to have a blend also with a more or less improved properties with a adhesive effect here, thermal property is reduced proccesibality is improved. Now that the it has been found that on blending of these two components, the transaction temperature T g of the blend is all in one.

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Although, there are two components it is up it is can be it can be expected that, if you take two component polymer say polymer 1 and polymer 2, they can have different T g, T g 1 and T g 2, but if these two polymer are compatible on blending. They will form a polymer product polymer blend P B, which will have only a single T g, that can lie in between this T g 1 and T g 2. This a only having only T g of the polymer blend, although polymers of 2 different T g are used, this give a good indication of miscibility of components in the blend.

That happens due to the additive effect, so here single T g increases with increasing polyether, since the T g 2 of the polyether is poly phenyl oxide is higher than the T g 1 of poly phenylene so on the increasing the polyether in the component in the blend. Though the final T g of T g of the resultant polymer increase with the poly phenylene component and in terms of tensile strength, however the polyblend is synergistic. Now, in these case also T g increase in these way the tensile strength gives quiet improved energy at particular as I explained earlier, what you mean by synergistic effect.

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Now let us look into optimum requirements of complete miscibility, since these miscibility is an important criteria to be developed in case of a polymer blend so we must also examine the optimum requirements. Now, a component polymers must have similar polarity, identity polarity means they must have identical, and solubility parameter or very close solubility parameter of the component polymers. Then the component polymers should be of low molecular weight these have high molecular weight the high, then the solubility of the component, polymer in the blend will be reduced.

Then there might be there could be hydrogen bonding, which is a which is one of the requirement, if there is a hydrogen bonding the secondary interaction between the component polymer again that is very good for obtaining miscibility. Other than hydrogen bonding the strong interaction may be say other intermolecular interaction molecule say polarized interaction or depolarized interaction or interaction this is also an another requirement.

So, most polymers pair do not meet this these requirements complete theoretical miscibility, having positive free energy of mixing, they tend to separate into two phases so these is these aspects should be kept in mind. Since, two component polymer cannot meet the complete theoretical requirement of miscibility, so we have to look into free energy mixing if the free energy mixing is positive, the component polymer will turn into separate into different phases.

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Let us proceed towards to other aspects say semi compatible part of the miscibility part of the card and need to explain the miscibility, immiscibility.

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Effects of slight immiscibility or semicompatibility

- Each phase will be a solid solution of minor polymer in major polymer.
- Phases separate into submicroscopic domains with the major polymer as continuous phase with major contribution to properties.
- Plot of properties vs. composition is S-shaped showing an intermediate transition region with a phase inversion from one continuous phase to the other.
- Most commercial polyblends are of this type, with the major polymer as continuous phase retaining most of its properties, minor polymer forms small discrete domains contributing synergistically to certain specific properties.

Effects of slight immiscibility or semi compatibility in these case each phase will be a solid solution of minor polymer, in major polymer, slight miscibility. They are slight miscibility or semi compatibility and they explained, if there is it is seen that each phase will be a solution of

minor polymer in the major polymer. Now, the phases separate into sub microscopic domains with the major polymer as continuous phase with major contribution to properties these resemble such kind of resemble filled polymer system, but the filler particles may remain dispersed in a continues matrix here, major continues phase of the major polymer.

They can the they may be some microscopic domains of the smaller components, and in these case these continues phase of major contribution to the properties. Plot of properties versus composition in this case is a s shaped card has you see from the card is a s shaped card showing an intermediate transition region here, a this transition region with a phase inversion. In that phase inversion from one continues phase to the other phase that means disperse phase would become, the continues phase and the continues phase will become the dispersed phase, this kind of inversion is a occurred to be in case of semi component blend.

Now, most commercial poly blends are of this types with the major polymer has continues phase retaining most of the properties minor polymer forms the small discrete domains contributing synergistically to certain specific properties. So, the major polymer contribute the major properties and the dispersed phase polymer disperse domain of the discrete polymer that contributes to the synergistically option of the some of the aspectic on some specific properties, special properties.

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Now in case of incompatibility the third component of the card incompatibility, here the less miscibility in case of less miscibility phase separation from larger domains with weaker interfacial bonding between them. So, here the domains, larger domains there can be domains depressed domains in a continuous matrix, now if there is some lack of interface bonding interface interaction between the domains and the matrix page, then we talk we regard this has less blend having less miscibility.

Now this happens due to the weak interaction at the interface and it there is weak and under stress the poly blend this stress will be concentrated and those interface and the poly blends the poor properties. That means the mechanical properties will be inferior and the product will fail at the interface at the weak interface side, and so poorer properties either of the polymer in the blend. Next this inspect card property card thus provide a strong indication of miscibility this is a curve gives a strong indication of in miscibility or incompatibility between the component polymer.

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They show practical incompatibility and lack of practical utility, now in these case of synergetic behaviour you see a synergetic behaviour, this shows improvement of properties beyond that expected from simple additive effect. So, if you draw if you combine this properties individual polymer, that is that is the additive effect, so this the they good visibility

and it is the effect of dispersed phase good interface interaction between the dispersed phase and the matrix phase. They can be some synergetic effect or improvement or increase in properties at some intermediate composition, the synergism may result from dipole dipole attraction between the polymer components.

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Now, the example of synergistic behaviour typical example of polymer blends, we can think of we can discuss with the blend of LDPE, Low Density Poly Ethylene with EPDM, now these can be good (()) of component polymers for making a successful blend. Now, LDPE contains ethylene unit, EPDM contain ethylene unit and propylene unit, so this suppose to form a good interaction between this poly ethylene will provide good interaction between this ethylene unit of the co polymer, ethylene propylene.

And since, poly propylene a propylene unit they also add on hydro carbons, so ethylene a segments of poly ethylene is also to have a good interaction with this poly propylene. So, this kind of blend E and ethylene propylene co polymer blend gives a good synergistic effect, and in these case the synergistic will further increase if this epidium part is epidium is partially crystalline. Poly ethylene is crystalline now ethylene propylene is amorphous that why it is rubber, now if some crystallic is developed is ethylene propylene domain so it will provide further synergistic effect.

Now if that crystallic could not developed if it remains has amorphous in this case amorphous, this epidium will show a non synergistic effect, so in order to get in order to obtain synergistic effect of this poly ethylene LDPE and EPDM blend. One of the requirement is that the epidium component should must be partially crystalline, so this partiality crystallity in epidium is a dramatic effect of morphology of properties of thermal blends.

So, this synergistic arise from a tendency of LDPE to crystallise and nucleate crystallization of ethylene segments in EPDM, is a very good interesting observation. Since, LDPE is in this line LDPE crystalline that LDPE crystalline will induce or nucleate some crystallisation in the ethylene segments of the epidium polymer, that why the synergistic effect is available.

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Properties of miscible polyblends
Physical properties of polyblends are
governed by the semiempirical rule:
$\mathbf{P} = \mathbf{P}_1 \mathbf{\phi}_1 + \mathbf{P}_2 \mathbf{\phi}_2 + \mathbf{I} \mathbf{\phi}_1 \mathbf{\phi}_2$
Where, P is polyblend property, ϕ is concentration,
l is interaction term (+ve, -ve or zero)
For I = 0, rule of mixture (additive rule) applies
For +ve I, P > weighted average of constituent
For us I D (simple sucress shows
For -ve I, P < simple average, shows
int synergistic.

Now the properties of miscible poly blend can also explained in other way this physical properties of poly blends can be semi empirical are governed by the situation P is equal to P is the overall property of the blend. That is equal to P 1 pi 1 that means P 1 is the property of this component one polymer, P 2 is the property of this component 2 polymer pi 1 and pi 2 are the polymer fraction of the two polymer and this is a pi 1 by pi 2, I pi 1 pi 2.

Now, plus I into pi 1 into pi 2 pi 1 into pi 2 where P is poly blend property pi is concentration and I is interaction term, so this interaction term can be positive or negative or 0. Now, if this I is 0 this term becomes 0 and in that case rule of mixture additive rule, additive effect applies, in case of the hallow I is positive in that case P would be greater than the weighted average of constituent polymers and that shows a synergistic effect. So, in case of positive value of I one can get the synergetic effect on the property of the poly blend, if the value of I is negative that is the less, then the simple average value of properties of the two components this shows the synergistic behaviour.

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In case of immiscible poly blend if there are two phases this phase 1, which continues phase 2 dispersed phase, but this two phases are immiscible phase there a semi empirical relationship can be used for explaining the properties of immiscible poly blend. That is P by P 1 is equal to 1 plus A B pi 2 by 1 minus b psi pi 2, where pi two is concentration dispersed phase component, and A varies between 0, and infinity depending on the shape and orientation of the dispersed phase, and nature of interface.

And B depends on the relative values of properties say P 1 and P 2 of the component polymer, and A of and an A P 1 and P 2 on A and psi reduced concentration, that is a function of maximum packing fraction. For A tending towards 0, the dispersed phase is soft or A tending toward infinity the dispersed phase is hard. So, the value of A and the value of B and the concentration of component polymer, that or the determined the overall property of P of the polymer blend.

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Now, let us look into the compatibilization of polymer to make a component polymer blend, now incompatible polymer blends are weak you know the reason behind this is that, there is that can be high interfacial tension between the component polymers. And at the interface poor addition it is found between the two phases, now blending of polymer that becomes unsuccessful that becomes due to the incompatibility of the component polymers. New successful polymer blend preparation, became possible by the use of compatibilizing agents, this approach yielded unique properties in polymer blends not attainable from either of the component polymers of the blend, their performance depends on the size and morphology of the dispersed phase.

Now, there are various ways of compatibilization, which are discussed on (()), say in case of biodegradable polymer people tried to develop bio degradable polymer from polyethylene. As such polyethylene is non biodegradable polymer, in order to make this polyethylene biodegradable people blended starch with this poly ethylene, but starch is a natural occurring polysaccharide, which was blended with poly ethylene. But, this starch is a poly polymer and

poly ethylene is a non polar polymer, the compatibility of these two polymer are most negligible, this two components are immiscible and in component in the blend.

In order to improve they compatibility people used malic anhydride grafted poly ethylene, has the malic anhydride grafted for poly ethylene and starch. Say 5 to 10 parts of dual parts of malic anhydride grafted PE with certain proportion of poly ethylene and starch could lead to a semi compatible poly blend of starch and poly ethylene. While, poly ethylene and starch are such are immiscible but huge of height obtained by parts of malic anhydride grafted PE improved they miscibility, because malic hydride part is a polar part that helps in interface addition, between the poly ethylene and starch forming the semi compatible poly blend.

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Now, in case of polymers as mutual solvents the other ways of this compatibilizing is some polymers as mutual solvents component polymers and in this case this polymers as mutual solvents are used has compatibilizing agent. For example this polycaprolactone is a poly ester biodegradable poly ester, this polycaprolactone when it is blended with polycarbonate and poly styrene co acrylonitrile such type of composition can be available.

Polycarbonate and poly styrene co acrylonitrile they compatibility can be improved by use of polycaprolactone, here the polycaprolactone has a solvent in this miscibility of the component

polycarbonate and poly styrene co acrylonitrile. Other example of such polymers acting has compatibalizer are EPDM Ethylene Propylene Dine Polymer which is a rubber, when maleic anhydride is grafted on EPDM.

That can be easily blended with nylon 6 6 polymer and this happens due to the drafting of maleic anhydride, otherwise the polymer nylon 6 6 is a poly polymer they are not supposed to be miscible with each other maleic anhydride is grafted EPDM this maleic anhydride in this EPDM grafted chain in the EPDM acted has the compatibalizer here you can say EPDM has been functionalized in such a way by grafting maleic anhydride so that it becomes miscible with nylon 6 6 before such addition with EPDM was not miscible with nylon 6 6 so the interface addition additional interface bonding of EPDM and nylon 6 6 can be improved grafting maleic anhydride on EPDM.

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Now, if we look into this scheme of such grafting reaction between EPDM and maleic anhydride the grafted this is grafted maleic anhydride part grafted on EPDM, that reacts with the terminal N H 2 of the nylon. This nylon consist of N H 2 group, so this anhydride group anhydride group is to act like acid these acts like amine group acts like this is a kind of acid base reaction and some condenses occurs and forming. This poly amide bonds to which amide

bonds with the end of the nylon thin and this is the EPDM chain, and leaving behind one free carboxyl group.

So, you can say these a kind of reactive compatibilization and many people have tried with different system and they found such reactive compatibilization are compatibilization, such kind of compatibilization through reactive blending gives excellent results in compatibility and improvement in properties of the poly blends. So, this is the EPDM chain to it maleic anhydride was grafted and this amine group of nylon chain, this side contains the rest of the nylon part residual part of the nylon molecule, so here yet through touch permanent covalent linkage kind of system is compatibilize. So, nylon 6 6 becomes compatibilize with EPDM with such (()) hydride grafted.

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Block or graft copolymer as compatibilizing agent

This type of compatibilizing agent reduces interfacial tension, alleviates gross segregation, and promotes adhesion.

The effective concentration of such block or graft copolymer range from 0.1% to 5%.



If we take this block or graft copolymer it is another way of compatibilization, we can take copolymers graft copolymer or block copolymer for compatibilization of two component polymers.

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Here, the presence of either of this graft co polymer or block copolymer can increase the interfacial tension between the component polymers and that prevents the gross secretion of the component polymers and promotes addition between them. The effective concentration of such block or graft polymer may range from 0.1 percentage to 5 percentage so this the presence of this block or graft copolymer reduces a miraculous effect in compatibilization of the component polymers in a blend.

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Let us look into some specific example for example, the component polymer to be blended may be designated has polymer A poly A to be blended with poly B (no audio from 33:16 to 33:32). For compatibilizing this two polymers poly A with poly B, you have to choose a polymeric compatibiliser of this form poly A block B means you can have a polymer having block of A monomer followed by block of B monomer. Like this A block B block and the base component polymer is made of A monomer, and this other component polymer contains B monomer.

So, the component polymers is made of A and B monomer and this two may not be compatible, but if this same monomers used for a block polymer. That block polymer comes between this A and B here and in between this A and B then B part, then B part of this block polymer will orient toward the B component A part will orient towards a component and that leads to miscibility between two polymer A with polymer B.

Alternatively, one can use the poly C block D or poly C block grafted g not block grafted g, so you can one can take A block of polymer of C and D and one can craft copolymer of C and D. At C and D are compatible with A and B C and d are compatible with A and B respectively, but are not miscible with them, so C and D are compatible with A and B respectively, where C and D are added to A and B respectively, but are not miscible with them. So, they can be added

but not miscible, but if this kind of technique can help compitabilizing of polymer A and B of polymers of A and B.

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Let us take the example of EPDM, PMMA blends, now this EPDM contains say the units like this ethylene unit with propylene unit and some diene in it.

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So, this is EPDM diene can be ethylene (()) 1 4 epidine, so and so this EPDM polar polymer and PMMA should this a polar polymer and this non polar polymer. This is EPDM is not supposed to be compatible EPDM is not supposed to be compatible with this PMMA, but that can be compatibilized, if on text EPDM such EPDM molecule to which suppose this is the EPDM having this kind of chemical formula, chemical structure on to which if this kind of polymer can be grown by grafting, so this is PMMA chain this is possible grafting of PMMA chain on EPDM.

While, EPDM and PMMA are immiscible non compatible, but use of small proportion of small quantity of this PMMA grafted EPDM, in between this two can produce a good compatible polymer polymeric blend. So, EPDM plus this PMMA grafted EPDM can mix with PMMA, now this PMMA grafted EPDM will orient itself with such a way that EPDM part will orient towards the EPDM. And here this towards PMMA, PMMA part will orient towards, if PMMA and this system enter system will become compatible.

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They can be other examples P P poly propylene, poly ethylene blend with EPM ethylene propylene (()) polyethylene blend is purely saturated (()) purely saturated tower without having a crosslink site. To make it cross linkable consider some theoretical cross linker to make to cross link it, this also an elastomere ethylene propylene co polymer or one can take

EPDM. Now, in this poly propylene and poly ethylene, although both are plastics but this two polymer contain different chemical units.

Poly ethylene is structurally symmetrical in one way and poly propylene is structurally symmetrical in other way, but if some poly propylene is some quantity of poly propylene is introduced in poly ethylene matrix of the vice versa. The crystalline property crstyalinity of the either polymer will be affect, has it found that propylene unit is co polymerized with ethylene, it will form a copolymer of ethylene and propylene is plastic, where has poly ethylene is plastic.

Same effect can happen over here, that means they can lead to a an incompatible blend or that can be made miscible provided some compitabalizer is used. In that case again this EPM or EPDM is a solution is develops compatibility, the reason is very similar either EPM or EPDM contains both ethylene and propylene in their back bone chains. So, this polymer segments will orient in such a way that ethylene units, will come close to the ethylene units of poly units and polyethylene such units of EPDM will come closer to the propylene units of poly propylene.

So, this a they form a compatible system of polymer plain, other example is poly styrene nylon 6 blend, again this are two extreme in nature. They compatibility can be improved by adding poly styrene and with A block copolymer of polystyrene and nylon 6, another example is poly styrene co polymer with actro nitryl poly actor nytryl (()), one component polymer. Another component polymer poly styrene co polymer with butadiene, so this component has polymer P 1 and P 2 that can form a very good blend, if one takes blends with butadiene or butadiene tower PPM block copolymer block of butadiene followed by block of MMA.

This a block polymer such block copolymer can act has a compatibilizer between component polymer P 1 and P 2, reason is styrene, polystyrene is rigid polymer rigid polymer which gas impact strength. Astyreyne leads to a very strong polymer strong and tap polymer and they rigidity can be modified the can be modified by dwelling with styrene butadiene co polymer this is a last (()). But, the miscibility is not available in order to increase the miscibility between the (()) polymer with the styrene acrynate co polymer, a block of methyl diene MMA co polymer or block copolymer of butadiene and PMMA, acts has compatibilizer to improve the properties.

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Now, they could be some modifiers, which as compatibilizing agent, that modifier can be interactive co polymer containing a rubbery component, say example is acrylic based copolymer chlorinated polyolefin's ethylene propylene diene poly ethylene co vinyl acetate etcetera. These polymers play a dual role compatibilizing and toughening, so since they increase they compatibility and allow it increasing the compatibility they increase the toughness of the polymer, this polymers are used at much higher loading than pure compatibilizers. Thus while 0.1 to 5 WT percentage compatibilizers may be sufficient, in this case 10 to 40 percent of the modifier may be needed to modify the properties of such polymer blends.

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This shows a scheme of the preparation of a polymer blend between poly carbonate P C with poly butylene tyralate, butylene tyralate is flexible where has poly carbonate is rigid.

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Now, here one can use 30 to 70 percent of poly carbonate and PBT can be use from 20 to 60 percent, in order to get high impact strength alloy out of poly carbonate and butylenes tiralate. The some core shell acrylic latex can be used to improve the impact strength of the two

component polymer in the blend. You know PET Poly Ethylene Terithylate is a poly ester PBT Poly Butylenes Terithylate is also another poly esther, and poly carbonate, that contains this carbonate group. In the polymer chain are being some rigid phenyl rings, this way so the presence of this unit presence of this unit makes a very good high impact property polymer and further its impact strength can be improved by blending with PBT.

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Now, they can be nano blends, now they dispersed the dispersed phase particle size in a blend is rarely below 0.1 milli meter or 0.1 milli meter or 10 nano meter irrespective of the compatibilization method. During extrusion processing during extrusion in situ polymerization of monomer A in the presence of polymer B can compatibilize to form nano structured blend processing. That means such nano structured blend can be keep a during extrusion polymerisation means, when two component polymers are extrurate by mixing in a extrusion screw, so these two monomers can polymerise.

During such extrusion and a fraction of polymer B chains bears initiating sites at the chain ends or along the chain back bones from which polymer a chains can grow. Basically, it is a kind of grafting reaction of one monomer onto the grafting of the main polymer, during the extrusion process because that free radicals which is required to create a grafting site. That free radical is create by mixing during extrusion and grafting in this process polymer A and a graft of block copolymer of A and B are formed simultaneously, leading to in situ polymerized and in situ compatibilized A or B polymer blends, the feasibility of such a process was studied for nano blends of poly propylene nylon 6.

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So, this reaction scheme sources graft copolymer of poly propylene and poly amine nylon 6 PA 6 using an isocyanate bearing poly propylene, here you see this is a polymer bearing an isocyante group. And this the capro lactone, this capro lactone can form nylon 6 by opening the ring at this bond, that means this bond breaks and breaking this bond it polymerises you see it need to be linked to this polymer chain through nitrogen leaving forming this amide link.

So, we find that we find that some acid acceptor can be used over there, and that continues to grow such nylon chain on the poly propylene back bone, so if this steps 1 and 2, 1 2 and 3, if this is this are the beginning initiation stages initiation steps. That can continue to propagate in the propagation state to form a polymer chain on poly propylene, that means poly propylene chain over which nylon 6 is grafted on this poly propylene chain. And ultimately, a blends of poly propylene with nylon 6 is available, this is a kind of thing some kind of which is which is totally impossible situation.

One can by grafting polymerization one can make impossible situation into a possible situation that means is poly propylene and nylon 6, are basically highly immiscible polymer, through grafting reaction during excursion process. Such good compatible blend of poly propylene nylon 6 developed by this process, and here shows the detail reaction scheme how this nylon 6 is reactive to this poly propylene, this is a kind of reactive blending in otherway we can say it is a kind of reactive blending.

So, in the long run if somebody wants to develop a property polar polymer on to proper non polar polymer this is the way how one can proceed, again if take the example of poly ethylene which is non biodegradable, but this poly ethylene can be made biodegradable provided some oxygenated of polar atoms groups can be generated over poly ethylene. And that polymer can that polymer can be bio degradable.

So, this gives an indication that the worst poly ethylene firms that can be collected from the garbage, cleaned and such type of reaction of some captrolactom or reactive monomers can be mixed can be excluded during mixing the polymer forms a grafted chain over poly ethylene. And that polymer can be used has a biodegradable polymer or biodegradable packaging firm, so one can take such a project of blending packaging, waste packaging firm with caprolactom or reacting monomer to form such bio degradable project.

Thank you.