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Lecture 31 Introduction to plastic and rubber mixing and blending

Welcome to the NPTEL online certification courses on the rheology and processing of paints, plastics, and elastomer-based composites. Today we are on week 6 and lecture number 6.1 and we will be talking about introduction to plastic rubber mixing and blending. And essentially what I am going to focus on in this lecture is understanding blends and composite and their fundamentals to engineering. So, the concept covered obviously will be first try to understand comparative way polymer blend vice versa composites, different types of blends their classification, visibility criteria blends, methods of blending, compatibilization, advantages composite or mixing of polymers together, advantages of polymer matrix composites, so composites over ceramic matrix or metal matrix composites and bit on thermoset versus molten thermoplastic in terms of the rheology basically. Once again the key words for your own self studies actually.

The most important part of it today try to understand the concept of UCST and LCST upper critical solution temperature and lower critical solution temperature which is the fundamentals of poly blends to foresee whether it is going to be miscible or immiscible in that sense. And then IPN interpenetrating polymer network that conception. Then differentials this will be differential scanning calorimetry or DSC and bit on the isotropy and anisotropy aspects. Now, let us quickly try to understand what is the difference between a polymer blend and a composites.

Polymer blend essentially is a blend which is a combination or mixing of two or more polymers which are physically mixed to obtained in a single phase. So polymer if you have two polymer you cannot say chemically two phases or three phases will be distinct. On the contrary polymer composites is a compound made by mixing two or more elements resulting in a multiphase distinct phases basically components system. So that is the basic difference. So polymer blends two components of it really a similar organic material while a composite you think about glass reinforced epoxy matrix then epoxy is a polymer glass is a altogether a ceramic material.

So that way they are chemically distinct as well as they are two different phases. So when I talk about polymer blend vice versa composites. So polymer blends consist of two or more polymers as I defined already. While polymer composites consist of polymer component and one component maybe non-polymery and it may not be a polymer at all when I talk about a metal matrix or ceramic matrix. So that is how it differentiate and polymer blends usually do not form strong chemical bonds between the polymers and polymer composites have a chemical and physical bonds most often with the matrix.

If the polymer is a matrix if you have a epoxy matrix you have a glass fiber there has to be some good interfacial bonding between the matrix and this part space or reinforcing part of it otherwise there will be a catastrophic failure happen. So in the whole a polymer plus other polymer and if it is another reinforcing agent that way it can be either distinctively polymer blend or in one hand in other hand it will be polymer composites. So you may add certain other ingredients say for example for a two non-compatible polymer system you add a compatibilizer you may make it rheologically more friendly you try to make it plasticizer or rheological additives and there are several other additives including the pigments and even deodorants also possible. So a unit process you will be following commercially is a melt mixing process. So in the molten condition you would like to see here this ingredient together in a confinement and then resulting in a homogeneous or it may be isotropic anisotropic depends on the composition you choose but is a mix you call it a compound.

So in polymer blend blends miscible polymer blend homogeneous down to the molecular level I mean then you take at any point you try to analyze the composition you end up the two component polymers at certain molecular ratio that you mix it only. So that is that there will be molecular level association and from thermodynamic point of view you get you have to have a negative del G. So that is the one part of it. So del G and del HMOI I am talking about because often in polymer blends entropy change is negligible unlike it is a simple molecule you mix them together total entropy gain delta S equals to xi ln xi this is a fraction mole fraction of two components that is going to be sum of I equals to one to whatever one to n. But if you in case of polymer since xi is very small molecular weight is very high in that way net resultant entropy gain is not that negative number so that resultant del G depends solely on your del H has to be as minimum as possible then only it will fulfill the criteria.

And the second derivative case should be greater than zero second derivative means second derivative of Gibbs free energy with respect to the volume fraction. So it is a single phase structure we are talking about so at the end if you end up mixing two miscible polymer you are having one T g only. You have mixed two polymer with two different T g but in a homogeneous system you will have a single T g of the system and Fock's equation will enable you to calculate what is going to be the resultant $T g$ at least in approximate sense. So immiscible polymer blends a blend exhibits more than two phases. So definitely you know even if you use best of best microscope technique like electron microscope you will not be separate between two domains for immiscible blend system but immiscible blend two components will be visible and provided you do requisite etching or staining of the phases otherwise you will not be able to see it of course.

Idealized phase diagram for polymer blend

So immiscible blend obviously other way round your del G is not positive it is not negative it is a positive Gibbs free energy as a result two you know component polymers conserve their own entity as a result you got to see two separate T g's if you try to monitor. So that is what it is this is the overall if I do not neglect the you know entropy

term but obviously as I mentioned it you this del H mixing actually if you just try to approximate it it comes out to be the difference between the solubility parameters of two components square basically. So your sense will be to make del H as minimum as possible it is anyway a positive number. So you want del G to be negative entropy slightly negative so your gain will be towards the negative del G value once the del 1 minus del 2 that is the solubility parameter of two component polymers we are considering two component system here the solubility parameter difference should be 0 as or in other words as minimum as possible at least to have a technologically compatible. In technological compatible blend means they will still phase separate but their domain size will be as minimum maybe in the nano or submicron size.

So in that case your difference of solubility parameter may be something positive but small number but ideal case it should be 0 for a homogeneous thermodynamically homogeneous blend system. So miscibility determined by the polarity difference between the polymer why I said solubility parameter again I am talking about polarity difference. See solubility parameter is actually sum of molar heat of vaporization and that what it estimates is sum of secondary forces acting between the polymer molecules basically. So that is how it actually has a sense of polarity higher the polarity that means solubility parameter is more reason why you know if it is a polar system dipole-dipole interaction is much more you know than that of van der Waals forces as I talked about hydrogen bond is even more. So sum is going to be eventually more for a polar system.

So that is how you can the thumb rules as I mentioned from the solubility parameter which is sum of secondary forces or cohesive energy density square or I mean cohesive density to the power half or you can say it is a indirect way of measuring polarity of the system. So the difference between that means delta 1 and delta 2 difference between the solubility parameter of two polymers is very close to 0.1 or 0 and 0 is the ideal case you call it a visible polymer blends. If it is 0.

1 to 0.25 in calorie per you know cc I am talking about then it is partially visible blend and often we call it technologically compatible blend this is also called technologically compatible blends like thermoplastic elastomer blends are actually technologically compatible blend system and then differences exceeds 0.2 why we call it invisible blend. So in the micron or sub-micron level there will be phase separation anyway. So when I talk about mixing two polymer what is going to be the morphology like it is like what if you have two polymer if I take 50 50 then what is going to be continuous phase what is going to be dispersed phase those are determined by number one the their volume fraction number two their viscosity ratio. So viscosity ratio why flowability one which can flow more than the other even if their composition is same so which flows easier or low viscosity will try to form a continuous matrix.

So there may be lot of morphological aspects I am not going into that details of it polymer blend as such is a subject of its own. I am just trying to give you the clues on fundamentals by which you will be able to at least penetrate and understand realize. So partially visible blends mixed phases with various polymer composition both single Tg distinct but approaches Tg what happened think about one polymer is having lower Tg another is higher lower means lower temperature higher temperature. Now as their polarity comes down solubility parameter difference comes down this Tg tries to come comes close close close close close and when it becomes zero then it becomes single out. So molecular wave what is happening you have a gross phase separation as Tg approaches or visibility more they are trying to be molecular wave single phase there is no interface between that before that there are some distinct interface.

So that is how morphology vice versa miscibility miscibility you conceive your idea. So miscibility gaps as a function of blend ratio and temperature of course the temperature will determine the viscosity of it. So three components three factors one is the temperature over which you are trying to mix these two components number two what is their volume fraction or ratio and number three what is the viscosity ratio. So grossly these are the thing determining the morphology of the system and where your Tg is going to be exactly located with respect to each other. The ideal case is these two merges into one that is the miscibility.

So now going further see anyway we need to understand a phase diagram like I said volume fraction so 0 to 1 one component over the other so and the temperature if you plot it you can end up having the phase diagram of a polymer blend system. So here you will see two distinct characteristics temperature here it is T4 and T2. T2 is called UCST T4 is called here here designated as T4 is the LCST. So in between wherever you always have a single phase so that means in between that condition at a given temperature conditions solubility parameter actually will merge. And otherwise what will happen it will be below UCST it will be unstable region so it will be you know phase separated region and in between there will be a metastability.

Let us say you get a you know morphology that morphology is not stable somewhere you can say metastable what is the metastability? See suppose you all know the minimum, minimum energy is a stable. So here is a potentially stable but somehow somewhere you will end up here in a small small minima unless you cross the boundary it is still stable but it is not absolute stable that is why it is called metastable. So this is these are the some of the thermodynamic construction I mean you have to go detailed into the you know this part thermodynamics aspects of it. In fact solution properties of polymers like PGA Flory you can say it is a Bible. And if you go through and through each step of it you understand more on solubility parameter, more on what is the chemical potential or Gibbs free energy how it is changed and what is the interaction parameter specifically.

As I mentioned once you have a two polymer in between there should be interaction. Interaction is less it will be India and other countries border where we do not have much exchange. So if it is a very good exchange like countries like Nepal with India say we do not have essentially a boundary, boundary is porous. So there will be sufficient diffusion of people across here sufficient diffusion of polymer across A and B between the boundary that is what the conception of interface. So in a sense if I have to make a true good engineering material out of polymer blends I have to strengthen the interface because interface otherwise will be the weakest part of the that particular component polymer blends.

So miscible polymer tend to phase separate at elevated temperature this LCST what I defined by the way it depends on pressure as well that aspect I did not talk about. So while you are mixing you make it at higher pressure then LCST will try to go up. So as a result what you anticipate a immiscible blend you may end up having a miscible blend. So similar so although on UCST that that effect is not very prominent like in like LCST polymer mixes would be miscible or would exhibit phase separation already upon lowering of temperature yielding UCST. So if you just lower down the temperature while mixing obviously from the phase diagram you know where you end up here.

So accordingly you can do temperature treatment also. LCST is quite common for polymer blends compared to UCST that is a very common feature and LCST 240 degree means if the blend is melt process above 240 degree phase separation will occur and UCST behavior may be observed only in the case of polymer segment lower molecular weights. So otherwise it is very difficult to catch hold of the UCST exactly where it is it will be not that prominent. So once again what do I mean by UCST upper critical solution temperature. Above is the blend source low miscibility to a high miscibility.

So low to high it goes across the UCST. This is this boundary part is single phase again. In case of polymers with comparable molecular weight the UCST is highest at 50 50 blend ratio. UCST also depends on the blend ratio also. And all other blend ratios UCST is lower.

So these are the some of the things again there is a very nice documentation you get it from the internet it is appended here. You can always consult that. Next stage is that polymer blends UCST versus parameter difference. Parameter is solubility parameter difference that del delta and you have a UCST here. See we have considered two

polymer blend system we have taken you know two rubber system.

One is polybutadiene and ESBR emulsor SBR another is emulsor and SBR two different emulsor and SBR. So magenta color is the blue color is the between polybutadiene and SBR. You see this delta delta difference between the solubility parameter between the polybutadiene and SBR is you know increasing with you know UCST. You can see the trend and the trend is similar but at a little different slope you can see for the other systems. So that way if you have this thing measured it is easy for you to predict while mixing or while processing at what temperature what type of a blend you end up with.

Whether it is a miscible whether it is a metastable or it is a very stable minimum energy and a single phase structure. So partial miscible blends can also show the miscibility changing over temperature and the most frequent case is observation of UCST behavior. So you can see the examples I was talking about miscible, invisible blends. See classically in polymer blend system there are very handful of polymer which are really miscible. Now if I just compare a polar combination polar polar combination by nonpolar nonpolar combination.

Nonpolar nonpolar combination is very difficult to have a thermodynamic miscibility. Reason you know reason is again del H part. Del H part will not be favorable that means interaction part. So interaction part is always favored for a polar polar system rather than you know nonpolar systems. So in that context I can tell you as a thumb rule that one rubber rubber system is miscible even like say you know butyl rubber and natural rubber although both are nonpolar but they are not miscible they were separate heavily.

And the case is more because solubility parameter difference as I mentioned thumb rule is 0.2. If you increase the molecular weight of the chain even a 0.2 difference of you know solubility parameter will yield you immiscible blend.

So those are the some of the funders. So polystyrene PPO is a thermodynamically miscible blend. See what happens polymer polystyrene although is not a polar molecule but PPO polyphenylene oxide is a polar molecule. But thing is that this aromatic ring is a commonality between these two and their interaction favors miscibility here. So similarly PVC-NBR is one of the classical system which yield you a miscible single phase system. So PVC-P, polyester, PET, PBT, PBDF and PMMA these are certain combination where.

But if I take the case of high impact polystyrene one or the classical one commercially exploited one this is nothing but polystyrene with poly butadiene certain amount of it is a class of immiscible blend where in a continuous polystyrene matrix you have a dispersed rubber domains and that gives you impact it is called impact toughening which polystyrene lacks in. So similarly polyethylene, polypropylene even though structurally they are very similar to thermoplastics but they forms immiscible blends. So distinctly they will give you two TGs. So properties of polymer blends may be intermediate between those of the individual polymers this is the additive roots. But in other cases the blends may exhibit either positive or negative deviation if I just show you what I mean.

See this is the property of A, this is the property of B. These two things are mixing a different blend ratios. What I expect the average additive this line should be the property. But it can be either synergistic, it can be more than that additive roots and it can be less than that.

So reason is that why it happens. One of the reason is see two polymer they are interacting each other so they have certain interactions donor acceptor think that way. But if it so happen in their combination in one case it is the donor another case the acceptor so you have more number of interaction between these two molecular chains as a result you have the synergistic increase of properties. So these are things you have to engineer eventually with certain amount of looking at certain amount of functionality. If that functionality is not present you have to augment with that functionality so that you have a more interaction and you have the synergism basically. So otherwise in a single polymer A and B whatever interaction is there that interaction diminishes in that case you do not get the additive properties it will be even less than that you can get somewhere here across the blend ratio.

So these are some of the things and some of the fundamentals are given out here. So determination of miscibility one is of course looking at the morphology. So second thing again it is not dynamic scanning calorimetry it is a differential scanning calorimetry DSC. DMA can be dynamic mechanical analysis can also because you will be able to capture TGs and from there whether single TG or multiple TG or even if two TGs how they are shifting and that shifting determines the increase interaction between these two domains basically. And then standard instruments in polymers polymer laboratories just monitoring the properties as I mentioned synergism means increase of the property rather than the additivity rule any properties can monitor.

Measurements the energy needed to heat it up that is heat capacity also is another way thermal transitions etcetera etcetera. So that way you will be able to monitor from the characterization point of view this is the example. So you have a DSC things two polymers if you mix it at different ratio PLA and PEG polythene glycol so this TG actually is simultaneously merging basically. So you see the TG of one of the dominant phase here you see TG of the another dominant phase here it is a so you can see this TG is getting somewhere in between. So it is a that way and same is the thing you can look it at what happened to the crystalline portion because we have taken two semi crystalline combination.

So crystalline structure also changes for amorphous polymers combination only TG will get it. But in case of you know semi crystalline polymer combination other than the amorphous part which is lost reflected from TG values but also you have another part which is the melting temperature or for here crystallization temperature. So one polymer can act as a nucleating side in that case your crystal structure will get refined. So as a result if you have a different crystal structure more than the you know its shift of TG the properties will be reflected because of the crystalline structure but that is altogether a different aspect. So methods of blending there are different techniques by which you can blend it but five different techniques melt mixing is the most commercially exploited one that that is what we are going to highlight over here.

Other than that there are solution blending techniques there are latex mixing technique particularly latex mixing is more prominent for rubbers but of course for other polymers also possible grafting is another technique to enhance the compatibility and the preparation of interpenetrating polymer network again it is a altogether a different subject different perspective two polymer intermingle intercross linked. So that gives you certain sort of attributes which are very very unique. So again looking at in a broader sense melt mixing solution blending latex mixing you know partial block or graft polymerization and then preparation of IPNs. Schematically the first one you either do it in a two roll mill or you can use an extruder or mixture you have a hopper and then you have a you know mixing areas where there it will be seared continuously and get the filament cut it and you have a homogeneously mixed system and you have a solution blended system you try to have it in the solution another in the suspension stage or both the solution mix together and then cast it let the solvent evaporate and leaving behind the polymer structure blend structure or composite structure there. Another is latex mixing of course to latex is also another kind of a dispersion but in a micelles basically and that has to be mixed you have to make sure it is stable and then you have to provide sufficient shear forces for the intermixing interpenetration of this and then you end up have a latex stage mixing.

Grafting again you can do it either in solid state just put some you know branch structure. So this additional branch structure what you will do if you have a two phase structure A and B in the interface we will have a improved interaction. Many a times you use di block copolymer as a compatible as there are or you in-situ in the polymer chain you try to graft it those attributes so that you have a increase like I mentioned donor acceptor sort of interaction host guess sort of interaction you have to improve upon. IPN is another concept it can be semi IPN or full IPN. In full IPN case two polymer network entangled structure together and both are cross linked and in semi you know IPN what you do one polymer phase cross link try to swell it with the monomer and try to polymerize it at this stage so in the network stage itself.

So this is called semi IPN which is cross link structure this which is solen and then eventually polymerize so it is a inter penetrating kind of a network it forms. So another it is another very interesting material that you have to really understand in the long run the advance studies. So compatibility means reducing interfacial tension improving interfacial adhesion basically and stabilizing the morphology. So these are the highlighted things three most important part for rest is written for your study purpose you read it here. And degree of compatibility between the components in the blends can be enhanced through the addition of compatibility there is a third party third party is given.

So this is the schematic one so there are different type of compatibility that actually improvises resultant gives free energy from you know positive to towards the negative side essentially it does that job. And you call it many a time rather than polymer blends polymer alloys alloy is the term borrowed from metallurgy I mean it is all the way same I mean as what I explained you so far. Interfacial activity is important polymers with polar groups as I mentioned interact with the components in the blend through non-monded interaction dipole-dipole interaction hydrogen bonding interaction that is the reason why it get component lies. It can be either chemically reaction between the two polymers or without the compatible raises another can be non-reactive also just using a block copolymer or a graph copolymer that stays in the interface as it stitches to which part of it you have a piece of cloth you have a holes you put a cloth and try to stitch it something like that engineering actually the compatible is the stitch in the continuous matrix of it so that way you can look it up. And chemical structure and interfaces of polymer reinforcement filler these are the some of the part the basis you choose it for and application limit that is also important temperature and the color stability also because color gives you aesthetics.

So, we are not going into those commercial aspects of it for the timing, but nonetheless various economic property has to be coined. See if you have to synthesize all together a new polymer it is a new technology you have to do many things, but why do not we have a with the existing polymer with judiciously engineering them so far utilizing the concept of blends and come up with the same property it will be more cost effective. So, polymer blends is more you know engineering way viable then again looking at the properties discover a polymer try to discover a polymerization process and come up scaling up. So, that is that is not that can be a long run process, but again polymer blends is very cost effective way meeting up all the properties you aim for. See let us take an example polyamide vice versa polyethylene some of the plus means positive attributes of polyamide 6 which is nylon 6 is it is a steep good barrier properties good thermal properties negative is sensitive to moisture.

While polyethylene you look it at it is a tough polymer strength is not as good as nylon 6, but it is tough that means it is elongation and break is more area under the stress strain curve is more actually. No water absorption or permeability processability is good affordable, but it swells to most of the you know solvents and high oxygen permeability. Now, if you can mix them two together you can you can have a better attributes. So, that is how you see you pick choose a polymer combination as far as you know composite is concerned you have two things one in one hand is matrix another hand is a reinforcing part as I mentioned it to you there is a major two components other than the minor components that way which part is a continuous matrix. If it is polymer continuous matrix you call it polymer matrix composites ceramic is a continuous matrix you call ceramic matrix composite metal is a continuous matrix you call it a metal matrix composite, but we are currently trying to focus on polymer matrix composites.

Two things isotropy anisotropy think about if we just try to put certain fibers in the in the polymer matrix. So, if this is the matrix and fibers are oriented in that at this direction. So, this way strength will be more than this way transverse way. So, if it is a x way it will strength will be more y way strength will be less. So, that is what is called anisotropy while you fill it with spherical filler homogeneously you end up having a very anisotropic properties.

So, again the fiber I talked about it can be long or chopped or short. So, short fiber will give you better process long fiber will give you better strength. So, it all depends what is your perspective whether the processability is the prospective or the final property is the prospective. Again in terms of filler it can be based on the strength and mechanical properties you have to pictures it can be particulate discontinuous or continuous fibers giving rise to SMC DMC or particular fiber based structures. I am not going into the details of the you know what are the advantage disadvantages, but nonetheless it is a light weight material that is why those are so popular in the you know even in the racing you know bikes also in a aero structure also aerodynamic structure also in automotive also high resistance to chemical corrosion compared to metallic counterpart even scratch resistance also.

Carbon reinforced plastics you know it is a material of the day to day. So, but that is altogether a different technology how you make a matrix and try to reinforce it for that. So, anyway the thumb rule is that stiffness of the reinforcement seeing unit should be more than that of the matrix otherwise it does not make sense. And it should have a good particle size shape as I mentioned particle size is too big surface area is too less then there will be flaws. There should be sufficient bonding or coupling between the matrix and the reinforcing units. So, these are some of the part mechanical properties depends on many thing orientation of the fiber size type design concentration dispersion and reinforcement and of course, it is just all the way same interface like in polymer grain case I told you to two domains one domain between that is the interface.

Suppose you have a fiber embedded in a matrix. So, these are the interfaces. So, how the fiber binds that is what it matters ultimately as far as strength is. Concern one important thing before we call it off. Suppose if I have a PVC that has a thermal stability window up to 190 degree stable. I have another polymer polyamide which has a window say let us say up to 275 degree centigrade it is stable on the other end polycarbonate is stable up to all the way 320 degree centigrade.

Suppose if I want to make a blend of PVC with polycarbonate. So, I have to obviously make sure that polycarbonate softens. So, if I have to really do mixing as 270 plus degree centigrade temperature PVC will degrade. But on the contrary if I look it at polyamide vice a vice polycarbonate we have still some overlapping window over which I can make them a good polymer blends basically. So, that is how its thermal stability plays very very important part factor. Even if you just try to look at very quickly polycarbonate T g of it or any transition of it how sensitive it is to the frequency.

So, while you know deforming it in a processing equipment. So, that T g also that that effect of frequency also can switch like unlike I talked about the pressure case on the LCST. So, similar so it will happen in terms of T g or in terms of softening temperature it will change quite a lot. So, frequency also plays very very important role here as you can see from the rheological studies here. So, this is what exactly it happen your stiffness versus you know see when the balance you know in the frozen in brittle state

how the molecules are there is no movement at all. So, only vibration is frozen in only molecular vibration is possible in that you know tuft or hard parts soft as rubber you have a you know sort of a random confirmation of the chains.

But while flowing after the crystalline melting the polymer eventually straightens up that you have to keep it in mind. So, let us take an example of PLA which is polylactic acid one of the degradable plastics biodegradable or degradable synthetic plastics. So, you see a chain extender is added a talc and cellulose fiber and basalt fibers are added. So, you can see is a PLA this is a control samples see what is CE is a chain extender what chain extender does it eventually increases the molecular weight if molecular weight increases what will happen this window will increase or its flow will be deferred that is reflected this to this. So, second one is just using little bit of chain extender and of course, little talc you have used then this started adding the reinforcing unit CF cellulose nanofiber and you know basalt fiber and you see that reflection in terms of dynamic geology.

And of course, the same is reflected for at different temperature as you can see for a you know thermoset by oxy resins also. So, these are the some of the way what I told you just give you a quick recap this you have to keep it mind while forming a blends polymer blends and forming a you know composite structure. So, this is these are the very important part for your realization just try to give you a quick recap about that. So, these are the some of the references that I already have given nothing new and in conclusion what we gave you is a basic conception on polymer blends and composites their difference how they are prepared and how you can engineer them to targeting a certain properties or certain processing attributes with that. Thank you very much.