Rheology and Processing of Paints, Plastic and Elastomer based Composites

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Lecture 27: Surface treatment of reinforcing elements

Welcome to NPTEL online certification courses on rheology and processing of paints plastic and elastomer based composites. Today we are in week 5 and lecture number 3. The title of today's section is surface treatment of reinforcing elements particularly of filler and chopped fibers. So, what we are going to deal with today is dispersing and coupling agent, dispersing agent and coupling agent what is the difference how it works. Silane coupling agent which is very common as I said with the particularly the silica fillers. Surface treatments of fibers, fibers means mostly of continuous chopped fiber as well as continuous conception will also be given.

Surface treatment of clay is used as a nano filler as well as a non reinforcing filler as I mentioned and sililation of silica filler which is a major focus of the day. Again for your studies these are the keywords you can always go back and try to read it and most important is the bound rubber conception of bound rubber which is you know related to the reinforcement. So, let us try to quickly look into that what is dispersion or dispersing agent basically. So, they are used to separate filler particles as I mentioned fillers in general have a very small size and therefore, the surface area is quite large.

So, they have always a tendency to form aggregate or agglomerate I mean secondary structure is aggregate and tertiary structure is agglomerate. So, dispersing promoter in a sense act as a wetting agent or sometimes like a surfactant they come in between two filler particulate and they will you know not allow the fillers to aggregate or agglomerate. So, therefore, in a sense it will try to improve the dispersion. I mean dispersion means once again coming down to the smallest possible particle size into the matrix. Now, coupling agent that the first thing dispersing agent is a physical effect.

It does not have a permanent chemical bond more often. It is a physical interaction I mean secondary bonds or secondary forces while coupling agent functions in a chemical route. So, what it has as I mentioned it has like a two arms. One arms catch hold of the silica particles or filler particle or fiber particle. The other hand will try to form a bond with a polymer matrix.

So, therefore, in that way they will try to always separate out the filler aggregates and they will reinforce basically. So, that is the essence of the bonding or bondability of a coupling agent that is being used. So, what it actually reflects means promoting dispersion or promoting you know by the aid of either dispersing agent or coupling agent. What is the reflection you get it? Rheologically the viscosity will go down because aggregated particles will always come as a lump and it will give a resistance to flow always. So, it will improve the flow once it is better dispersed.

So, therefore, if you think from the processing side or fabrication side or manufacturing side it makes easier to process it to give a better aesthetics of the finished products in essence. And in property point of view what will happen because of the reinforcement as I mentioned impact strength will go high all the failure property will go high. If it is a plastic then this sort of a dispersion will help in yield strength, elongation at break. Higher tinting strength for the paints or pigmentation point of view and enhance aesthetics like I mentioned because flow is better die swell is going to drastically reduced. So, aesthetic or finish will be better and block filler surface cannot absorb additives from the polymer that is another problem.

Say for example, if you have excess silica in the system it will always have the affinity to absorb some of the curatives you know some of the accelerator activators. So, therefore, your polymer will stir out of those agents. So, once you coupled it once you have a surface treatment of it. So, it will not be able to adsorb any further. So, therefore, it helps that way as well.

So, you can see schematically the first one elaborate schematically the dispersion. So, here you can see between the polymer and the dispersing agent I mean actually anchors to the filler basically and it has the another part another part is kind of a you can imagine like a steric hindrance it will flow by. So, that it will not allow I mean within that space the another part it will come therefore, it will prevent the aggregation. On the contrary what coupling agent functions in one hand like I said it forms a you know link or anchorage with the filler surface they have a sufficient buffer point or for the flexibility sake and the other end other arm try to capture a polymer chain. I'll show you in detail mechanism particularly silane coupling agent which is more popular from that structure point of view I will show you a little later.

But nonetheless for the time being schematically if you look it at see in one case you have some spacer, spacer is nothing but the dispersing agent more often it's a surfactant kind of a molecule. So, it can by ionic interaction hydrogen bonding interaction I mean depending on whether cationic anionic or neutral your surfactant is depending on its head functionality and functionality on the top of the surface it will try to interact giving rise to some spacer behind like he said this is area will excluded I mean another particle cannot peep in and stay there. So, therefore, it forms some sort of a then next in the vicinity this part will try to interact with the polymer chain. So, therefore, you can see in a sense your dispersion improves. On the contrary if you can see other cases, this coupling agents are sitting out here and then try to anchor and form a permanent bond with the filler surface.

So, this is the two way you can visualize in the you know in the field system how it stays. So, there are many examples many types of surfactants or dispersing agent or coupling agent. But as I mentioned when I you alter the coupling agent it is more relevant to organosilanes for silica coupling other than that few of the organometallics including titanates zirconates aluminates are often used. But most importantly from the point of view of dispersing agent those are metal salts of fatty acids. So, acid functionalize polymers is a fatty acids like zinc like stearate odeate and zinc salt of it may be sodium or calcium salt of it.

So, it can be hyper dispersion as well you know polymer can be a good surfactant of course, the low molecular weight side highly bronze type of a architecture will give you some dispersion effect those are also used parallely and waxes is a small olefinic units which can often be used as a you know dispersion promoter. So, if you compare a natural polymer say natural rubber vice versa synthetic polymer natural rubber in addition to the polymeric stuff you have some of the ingredient already inbuilt there. So, you may not have to add as far as carbon black dispersion is concerned you do not have to bother about carbon black goes well without adding any further dispersion promoter. So, that is the beauty nature to nature I mean that is how nature manufactures. So, now if you look it at several types of you know fillers and their corresponding dispersion aids how you pick choose case to case.

Like say calcium carbonate if you choose it see succinic anhydride is generally the best one found to be the best one, but of course, the second best will can be a carboxylic acid can be a primary amine you can see both acid and amine they can donate or anhydride they can donate the you know lone pair of electron and therefore, the bonding happens. Dolomite again the you can see the sulfonic acid sulfonic acid base surfactant as you all know there are different types of sulfonic acid base surfactants. Carboxylic can work and succinic here succinic comes as a third best here by the way. So, magnesium hydroxide, mica, talc so you have a several such functional material of your choice, but talc onwards which is a natural silicate mineral basically you can see silane works good. Well silane is the die agent for like trichlorosilane here we are talking about from the point of view of dispersion not from the point of view of coupling agent although.

So, here trichlorosilane works very good and therefore, and you know titanium dioxide which is often used in paints as a you know to mask the color of it because it has a high refractive index it is often used as a pigment. So, succinic anhydride works very good. So, depending on type of functionality you have type of mineral filler or carbonaceous filler you are choosing of dispersion agent will be different although I am not going to discuss about the rest part of it like the fatty acid part of it I mean how many carbon chain. I mean that also all together a different ballgame, but nonetheless I am talking about only the head group that is going to find the bonds with the filler surface. So, let us try to understand how this is most important the other part how the coupling agent works.

See coupling agent essentially I am talking from the silane point of view silane based coupling agent you have a silica and you have some piece array as I mentioned it to some that gives you a flexibility. Why flexibility needed that flexibility will allow you to find a bond from here to here to here otherwise if you have a rigid link it is restricted whole lot restricted to a particular direction. So, that is what how it works. Now this x functional group depends on the type or variety of interaction you want it can be a vinyl group, it can be epoxy group, it can be amino group, it can be in a mercapto group or sulfur simply. So, that way the other part of it it is silicon OR OET or OME type of a group you have.

So, it can this part essentially can condensed with SiOH group which is present in silica surface liberating one molecule of water and setting up a silicon oxygen silicon bond. So, that is the one part of it where it finds a bond with the filler site and this x will often try to find a bond with the your you know polymer chains like if it is sulfur or mercapto groups as you can know it'll be very well it'll try to form a bond with the allylic position of the you know carbon carbon double bond. So, that way your silica is essentially getting bounded through this coupling agent to the polymer. So, there are lot of varieties given here. So, reactive groups that forms chemical bonds with the inorganic material including glass metals inorganic.

So, you can understand this diversity of it I mean various type of filler, material not only it is restricted to silica you can use it different type ethoxy type, dialkoxy type, trialkoxy type again once it eliminates I am sorry I told water it one molecule of you know alcohol goes out. So, depending on the volatility depending on you know it is environmental hazard this R group you can pick choose basically. So, I am not going into that details of it, but again it will be shared with you in due course. So, resulting property like some of the important property whether to be rest assured my filler surface is enough enough you know surface treated. So, suppose if you are trying to make it hydrophobic.

So, that hydrophobicity one of the parameter. So, dispersibility another check your flow ability can be another check and of course, you have to really see whether high loading how it is sustaining giving a I mean small loading it may work well, but high loading once again will give you you know agglomeration problem. So, that you have to choose it I'll see to it. So, before treatment you see the filler as a SiOH group and that if you once you put in silica as I mentioned it to you I mean it forms a bond with silica and this X group is you know free to form a bond with the polymer chain of the matrix. So, examples are plenty as I mentioned it's not only restricted to silica you can find you know in talc, aluminum hydroxide, titanium hydroxide, titanium oxide everywhere it can work well.

And many of the silica by the way are sold or already pretreated way it is already sililated. So, you can put it can go it go better than that of the non treated one. So, here in that SEM photo micrograph you can see in one case the silica particles you can see they hardly have any bonds with the you know matrix, but second, one sees almost buried it is a covered up the surface is covered up by the you know matrix polymers and therefore, in between them is the coupling agent sitting out there. So, that is how it works. So, you can see once you have a rubber matrix, fillers in the form of course, close to aggregate it has a secondary structure I mentioned it to you especially if it is carbon black or silica.

So, what happens your some part of the polymer chains is getting immobilized because of this sort of interaction for carbon black as I mentioned already you have a COOH, lactam other groups. So, it is having a during mixing it is several times bonds you do not have to add what is way about the you know coupling agent here, but for silica case once you add a silica do the reaction in the base catalyst reaction then it finds a bond. Now, some part of the polymer chains are really really embedded even if you try to extract it with a good solvent it would not come out and that particular fraction of the rubber is called bound rubber and as you can see some of the rubber finds its way in between the filler aggregate. So, imagine one thing once you are trying to deform it say occluded rubber which is sitting in between that hardly gets affected. So, therefore, occluded rubber has no role in the reinforcement.

So, your bound rubber actually is giving the you the reinforcement. So, you can do one quick test with the extraction figure out how much is the bound rubber in a rubber if you have a bound rubber content more that means filler reinforcement effects is going to be more ok. Of course, there are some sort of a quantitative equation like Krauss equation is one of that sort you can see a check it how much is a you know reinforcement you are getting out of out of it, but of course, for silica in its pristine form if you put it in natural rubber you put it in SBR it would not form a bond, bound rubber is going to be nothing almost negligible, but once you put coupling agent do coupling reaction. So, same effect what naturally happens with natural rubber or SBR with carbon black and that is going to happen in case of silica. So, that is the that is the role of the coupling agent definitely whatever deficit you have in case of silica filler that that you are going to make it up.

So, filler surface treatment you can do it in the wet method as well as dry method as well. So, methods I am not going into the details of it, but you can you can always go through sprawl through the schematics a schematic way and it can wet treatment enables evens treatment because it will engulf the whole surface together. If you do dry treatment it can be some part some part will be starving productivity is low because obviously, I mean there is a you know if you do wet process additional step you add on there. So, silane containing waste will be fluid must be dispersed. So, what you do in order to wet the whole surface you have to dilute the silica may be in the alcohol or may be in the water that has to be you have to make it a point it goes off end of the day because otherwise it will give you a porosity in the fill system.

So, that way your dry process is better, but again productivity is higher, but many a cases it may starve as I mentioned to you. So, resulting property, so dispersibility that you have to choose it, it's flowability, rheologically, of course, you can monitor. So, that's what the essence of it, I'm not going into the details. Of course, the fiber you know many a times not only you use a chopped fiber, but also use a continuous fiber may be in the form of a cord to reinforce rubber because rubber as such has a very low strength. You can use even a woven fabric also not only the cord not only the you know yarn.

So, in those cases say for example, classically people started with you know cellulosic fibers, but went to its low tenacity and high you know density of it the people switched to you know synthetic fibers like a nylon and polyesters are the most popular one. But point was how to find a bond with nylon and polyester cellulose finds that bonds very easily cellulosic fiber because they can go mechanical interlocking because they are staple fibers. Once you make a you know from filament to yarn they have lot of protrusions there. On the contrary you making by you know spinning process there you know roundedness is much much more for the synthetic you know filaments and therefore, when one once you you know twist it you do not have that much of roughness. So, mechanical interlocking is out of the question.

So, what we want to establish in these cases again to add like a coupling agent it is not a coupling agent or bonding agents some sort of agents. So, like a RFL, Resorcinol Formaldehyde or sometimes isocyanate. So, those are actually treated and dried and before you use it to form a bond with the you know rubber matrix. See for nylon case it is a one step RFL dipping process, but for polyester it is even difficult you have a always have to have a two step process first isocyanate then you can go for the latex dipping technique. So, these are schematically elaborated those are actually adhesive or bonding agents for the textiles.

But of course, aramid which apparently more stronger aramid has its own disadvantage in terms of finding a very good bond with the rubber material not only that it has a self abrasion is quite quite high. So, mostly for the as far as rubber reinforced rubber is concerned coating on the fiber is mostly concentrated on nylon both nylon 6 and nylon 6 6 as well as the polyester and or their combination essentially. So, I am not going into that details you need process, but you can always see from the spinning to making a fabric to making it a surface treated by a process of dipping is elaborated in this here. Even it is a glass many a times you use a glass fiber also glass also needs to be surface treated for glass case your sililation will work well. So, I am not going into the details of it, but again resorcinol formaldehyde I already elaborated you when while talking about the basics of it.

And similar you can either go for novalac or you can go for you know resolve sort of a root and you try to have a surface treatment. So, that is how you do. Epoxy treatment is also often practiced these days with the you know aramids or aromatic polyamide specifically. So, now let us put our attention back into the filler system. Briefly we diverted little bit on the fiber part of course, in the fiber part also if it is a chopped fiber.

So, you may want to do either to novalac or resorcinol type of a treatment or also you can use some of the fatty acids also to treat it well to make sure the chopped fiber disperses well through and through with the homogeneity without any anisotropy into the matrix. So, surface treatment of the clay is a similar to that of the coupling agent shown schematically. So, if you imagine if you have a silica in one end SiOH group OR group in the one end in between you have a sulfur and then again silicon. So, what will happen it will break apart the sulfur will find a bond easily with the matrix polymer another end will catch hold of the other surface of it. So, that is the thing although there are different generation of coupling agent silane coupling agent I am not going to highlight just briefly to tell you.

The first one started with TESPT which has 4 sulfur in its structure. Then people immediately figure out it gives a scorching problem. So, people switch to TDSPT which has sulfur rank 2 that reduces the scorch but not whole lot. Then people started thinking of blocked Mercaptan-based silane coupling agent where at the temperature of mixing and processing it does not give a scorch problem but at high temperature this block thing opens up and gives you the sufficient bonding as you as you want with the rubber matrix. So, that is the genesis of different types of coupling agent you have it in the industrial practices basically.

So, surface-treated clays have had their surface chemistry modified as you can understand it becomes quite hydrophobic there. Otherwise you know silica silicate has a very high surface energy polymers on the contrary has a very low surface energy. So, they wouldn't actually I mean they will always try to form a aggregator there that is a natural tendency. So, by coupling agent dispersing promoting agent you are making it whole lot hydrophobic the clay surface or mica surface. So, therefore, it can disperses well into the kaolin clay same chemistry it has quite lot of SIOH group.

So, as you can understand you can you can established it in many a times actually with the cationic surfactant also you can achieve particularly the foreclay initially it started with the you know ammonium salt of I mean different alkyl chain higher alkyl chain maybe at least more than C8. So, that will actually give a space and clay structure has a stack up card type of a structure. So, it goes in on the surface and tries to have a steric effect and try to you know expand the layer space and then therefore, polymer can enter in p-pin. So, that in a sense it like a stack up card it will open out and it get dispersed that is a whole story about the nano clay. So, again for the calcium clay also water of hydration in kaolin is about 14 percent heat treating or creating eliminates the water.

So, if you eliminate water definitely it has a tendency to zip into the you know consolidate in the of the stacks. So, in those cases also you can sealant treatment can be a good solution as you can see. So, otherwise if you pull lot of clay into the system it will have a tendency to absorb or adsorb other other other effective ingredients including antioxidant activator as well as the you know accelerators from the system even it will absorb the sulphur the which is vulcanizing agent. So, this is how it is whole lot established. So, once again let us try to go through the chemistry here.

See with the base it actually RNH2. So, this is the thing then TESPT this is the structure it into symmetric as I mentioned to symmetric silicon and then it actually finds a bond. So, it will find out another silicon particle here similarly and then this particular part will find a bond with the rubber chain this is the rubber chain. So, this is silanization, but it is a base catalyst reaction basically often DPG is used today DPG is banned. So, different type of hexylamine or other amines people are trying to use it at least SiOR group from that SiOH and then final condensation reaction it establishes.

So, this is schematically. So, silica without apparently coupling agent it is difficult it aggregates, but once you have coupling agent it sufficiently form a bound rubber the ring of it and inside out what happens thus the coupling agent sits out here and tries to establish bond between two apparently separated you know entities. It is just like a border of two countries. So, in between if you have a quite good exchange then you do not have a tension and if you do not have a exchange then you have a worse situation. So, that is what it exactly amounts to. So, basically TESPT does its job and same as the NXT is a latest generation silane by Momentive here and that is how actually the chemistry revolves around all this TESPT VTES is a vinyl functionalized and this is the blocked silane also Si363 they are the different things, but activity is same.

The only thing is that as I elucidated TESPT to TDSPT to other Si363 to NXT all are to ease out the chemistry and risk of the scorching basically, but in a sense what it does it does it promotes the dispersion. So, essentially this is what so you go to any good standard textbook that deals with you know fillers and reinforcement you will find all those basics, but at the end what I try to give you the idea if you put in filler and that is the most largest quantity of additives you ever used in the polymer. So, that essentially unless it is dispersed unless it is properly treated it would not give you much sense. So, just putting any mineral say sand adding sand to the lava matrix it would not work because it will add on certain concentration point it will aggregate and your property will go down. On the contrary if you reduce the particle size significantly if you have a good surface chemistry I mean tailored on the surface and then you have a judiciously chemical treatment and then it goes well it reinforces it makes your processing also better it reduces the dIe swell the finished product will have more better aesthetics.

So, you gain from all point of views. So, these are the some of the books I already give you given you references quickly to conclude what I talked about at least you must have understood the sense of dispersing agent, coupling agent although both are used to promote dispersion, but dispersion agent from the principle it have finds a physical bond physical mode of modification well coupling agent is definitely there will be a chemistry involved here in this case sialylation chemistry I talked about sulphur it forms a bond with the you know rubber hydrocarbon chain that I elucidated. So, from the point of view of silane coupling agent weight functions and surface treatment of fibers I talked about, but only for the continuous fiber, but also chopped fiber also if you put it again fiber has you know more polarity. So, it would not really go very easily into the amorphous rubber part. So, you need again need to reduce the tension between these two interfaces and that you often establish with adding either dispersion promoter or by adding coupling agent coupling agent will give you a precise and better you know dispersion in the system for sure. Surface treatment of clays or any silicate minerals will be same to same and sililation of silica filler I have given you example how it works.

Briefly talked about various categories of you know silane coupling agent including TESPT, TDSPT, NXT, SI you know SI69 STSPT and then next variant of it is a 363. So, accordingly it is taken care of the scorching problem as well as ease of coupling basically. In the upcoming classes we are going to highlight the rheology of elastomer because you might have understood by now once you fill it out, disperse it well your rheological properties will change whole lot. It will increase the viscosity, reduce the di-swell.

So, let us try to see in from that next class how it works. With that thank you very much.