Rheology and Processing of Paints, Plastic and Elastomer based Composites
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Lecture 26 : Properties and role of various compounding ingredients

Welcome to NPTEL online certification courses on rheology and Processing of paints, plastic, and elastomeric-based composites. Today we are in week 5 and lecture number 2, the name of this module is properties and role of various compounding ingredients. In fact continuation of the where we left last 5.1 module. So what concept will be covered here is the role of fillers, fillers classification, filler effects, Black fillers which is the major filler in rubber system, Non-black filler mostly dominating by silica. Then off course there are certain other fillers also.

Reinforcement concept, fibrous fillers, nano fillers also, These days nano word has become a popular term although carbon black traditionally has been nano although it was not got the credit of name of nano but off course nano clays, graphene you know even carbon nano tubes and carbon dots, Those are some of the new nano materials popped up over few years. Then we will of course, try to talk about the process oils, plasticizer, tackifier, which are essentially a minor, but important from the rheology point of view as a rheology aids also like tackifier indeed improves the I mean tack and adhesion properties. Once again you can for a self study you can look through all this keywords that will take you to those conception like reinforcement, particle size. Most importantly two effects that I will elaborate today payne effect and mullins effects related to filler reinforcement, filler-filler interaction, filler polymer interactions then hydrodynamic effects, storage loss, modulus and shear stress, shear rate that you are already familiar with.

So, let us try to see what filler does so far. The vulcanizing agent which I talked about on an average it was limited to 5 PHR. See sulphur how much we used you remember it is 2 to 3 PHR at the most. And then you know your accelerator again 2 to 2.5 PHR it is limited to that.

Zinc oxide maximum 5 PHR and today it is 3 PHR only and stearic acid earlier it is to be you know 3 PHR it is now 1 PHR. So, you can understand those vulcanization aids were of the tune of limited to 5 PHR or below. But which is after rubber the majority major ingredient is a filler which is, which may be sometimes as same as that of the rubber used and many cases even more than the rubber the filler is the dominant part of it it is also possible. But particularly some rubber based system like EPDM, polybutadiene. they can easily take 2 times 3 times of the weight of the you know rubber matrix.

So, most of the rubber fillers used today has some functional benefits that contributes processability, strength of the rubber products. And styrene butadiene for example, has virtually no commercial use as a unfilled compound. So, SBR system you see I mean natural rubber still in the latex product you have a unfilled system you can think of, but SBR system it is mostly filled system only. So, let us try to quickly see look into the filler classification. In terms of reinforcement let us try to understand what is reinforcement means.

See if you fill certain polymer including rubber with some filler what do you expect to see hardness increases, modulus increases because of the hydrodynamic effects. But for reinforcement any reinforcing filler must improves its failure properties, wear and tear then only you call it a reinforcing filler. So, based on its function you can say it is a reinforcing which improves the is partially improves, you call it semi reinforcing and which actually deteriorates properties particularly failure properties are considered to be non reinforcing. Now, based on the color because carbon black as I said is a dominant there are wide gamut of carbon black categories of fillers available. But nonetheless those are carbonaceous in origin and there are certain fillers like silica silicates based filler which is non black.

Now, the question is that why should I go for non black? See if you have a non black filler system then you can afford to have a color to the product that apparently you cannot do for the black that is why your tire looks black only is a big truck tire if you happen to make it a colorful it can be a fashion altogether fashion involved there and you could have fetching lot of money. But unfortunately because of some of the attributes of carbon it cannot be substituted. So, for example, its thermal conductivity, electrical conductivity, UV resistance along with the reinforcement attributes of carbon black that makes it practically you cannot substitute it with anything even silica people are trying to make it 100 percent substitute. But still some way or other you cannot today up to today see colorful truck that bus tire maybe in a bicycle tire you can see still colorful that too a part of it not fully. So, reason is that you know thermal conductivity, electrical conductivity, UV resistance and on top of that the high amount of reinforcement.

So, one basic thing you must understand what your structure of polymer is, it is a carbon hydrogen and sometimes if you have a double bond that carbon black hydrogen is not that plenty it is a dominated by carbon and if you have a carbon black it is a similar structures. So, they have more interaction and your reinforcement comes from the interaction between rubber and filler, larger the interaction between rubber filler reinforcement is going to be more and more. Again I will come back up to the theory of reinforcement, but another part is also important not only type here black or non black, but also their shape, aspect ratio a particulate has a lowest aspect ratio a high bus material has a high aspect ratio that way if you consider you know a platelet type of a structure aspect ratio is low, but one way you can consider aspect ratio is actually high. So, actually with the aspect ratio L by D if you plot it comes you like that. So, here you have a platelet which is high reinforced surface area by volume, area by volume signifies that how much it interaction will have with the polymer and this is L by D ratio your sphere L by D ratio is one comes minimum even though surprisingly enough, all the carbon black fillers practically the primary structure of it is like a spherical and here you have a fiber L by D ratio is higher.

So, you can understand to have a increased improved reinforcement practically you must have a high L by D ratio platelet still this length this diameter thickness you consider otherwise on a fiber way if you think of it still high L by D ratio that of course, to give you more surface end of the day. So, this is the theory of reinforcement related to the shape of the filler. So, as I mentioned particle size matters as you at a constant volume or constant mass if you decrease smaller and smaller particle size you end up generating more area more is the area it has more chances to interact with the your matrix which is nothing, but a carbonaceous material again CH2 CH2 or C some are double bonds etcetera whatever structure it has. So, particle surface area plays very important role pivotal role as I mentioned shape also place, but the last thing with what I have not uttered yet is a surface activity. So, if you on the surface if you have a favorable functional groups like say OH, lactam, carbonin.

So, they can interact with your double bond present in your structure or functional group present on your polymer backbone and therefore, it gives you more filler polymer interaction and more will be the reinforcement. So, without giving into depth of it there are lot of theories related to, but there is a thumb rule, particle size up to 45 nanometer is reinforcing. Now, 45 to 100 or 90 typically nanometer primary particle size if I consider it spherical sort of a shape. So, up to that it is called semi reinforcing. So, what if above 100 nanometer or 0.

1 micrometer it becomes non reinforcing or dyed wind. So, the property will reduce it will act as a flaw point catastrophic failure will happen from that point. So, this is the basic understanding. So, this is how we can see there are other fillers also barite, barium sulfate, talc, calcium carbonate again you can scale it down to the size. See 45 nanometer roughly about is a scale here you get the reinforcement, what are filler you get it precipitated silica, fumed silica.

So, major reinforcing filler other than carbon black is siliceous silica base material. I will come back there and you have all the gamut of carbon black here which actually essentially gives you sort of a up to say 550 you can take it stretch it. it gives you know sort of a reinforcement. And then semi reinforcing meant see calcined clay, it can be again hard and you know soft clay what is hard is it really very hard "no". It is a particle size smaller size it is called hard.

So, this is grossly used in you know shoe industries a lot practically. Then you have a calcium carbonate which is wet and soft clay you can see gradually. we are going towards the non reinforcement and also the barite can calcium carbonate, those are diluent type of a filler this will not improve the properties, but it will just restrict the cost of it because those are less expensive material. Although calcium carbonate today you can get it in the form of you know nano size, zinc oxide which is apparently in the non reinforcing sort of a filler, but still you can afford to have a zinc oxide nano filler again you have to afford more energy there. So, therefore, the cost is going to be high.

So, this is the basic understanding the surface area as surface area increases of the filler, considering a favorable interaction with the matrix. Mooney viscosity is going to go high, tensile strength is going to go high, abrasion resistance is going to go high, tear strength is going to go high, hysteresis of course, this is the conception if you have a more filler in the system. See if I consider a carbonous chain polymer chain I mean elastic chain that is more resilient. you to come back hysteresis will be less, but if once you put a filler particularly if it is reinforcing type of filler there will be additional friction happening between the you know filler and polymer chain giving rise to more hysteresis and more heat buildup that is a conception. Increased surface activity as I mentioned you can see this surface if it can reacts or interacts with the you know polymer surface more immobilization will happen on the polymer chain.

So, therefore, is a reinforcement effects will happen. So, already I talked about the aspect ratio effect as you can understand, if I compare within a given mass of that thing if it is a spherical by say by cylindrical will give you always higher reinforcement. So, is a carbon nanotube case you gets better reinforcement. So now you see this properties how it effects I do not have to I guess, I do not have to explain you what is 100 percent modulus, 200 percent modulus, 300 percent modulus, it is actually the stress value at a given elongation that is a conception in rubbers. And if I consider a modulus then you have to refer to a young's modulus, which is within a limited elongation may be less than 5 percent elongation you have to stress-strain curve you try to take a slope of it.

But we hardly use the young's modulus for rubber rather than we go for 100 percent modulus 300 percent modulus means which is a essentially not the modulus in that sense it is actually stress value at a given elongation. So then elongation at break I mean you stretch it stretch it the point you note the stress where it breaks basically. And so is the you can understand now if you have a more and more and more anchoring of the polymer chain immobilization of the polymer chain on to the polymer you know fill a surface the more and more amount of immobilization happening. So that much of polymer chain will not be allowed so easily to elongation it will resist the elongation. So you can understand flow can be heavily heavily hindered a filled material case.

But again if it becomes non-reinforcing in nature say 50 nanometer and above, those can give you some additional ball bearing sort of effect. So it rolls on top of that the rubber can roll through. So therefore, total strain energy total effective strain will be less so die swell will be less. So you get a very very good surface texture. So I am not going into the details at this stage but nonetheless, if you just consider two major failure properties that often we consider is a tear and abrasion.

So more the bonding between rubber and filler more the you know surface area, more active functional groups you have you get the tear strength increased. But within a given you know surface area L by D ratio may have a negative effect also. So otherwise L by D ratio as I mentioned if as far as increment of the surface area is concerned. it will always give both tear and abrasion properties it is a plus for that. But of course a large particle poorly bonded filler abrasion will never improve, although it will increase the modulus and hardness of the material.

So increase of modulus or hardness is not the clue or is not the characteristics of a reinforcing filler. Reinforcing filler characteristics is that it must improve that failure properties. Fatigue it can improve the you know propagation of crack through that matrix. Abrasion, tear those are the point you can understand. Then if you load more and more filler what can be the situation.

So reinforcing filler you are adding up to certain point definitely tensile strength will improve, which is also a technically is a failure properties basically because tensile strength is strength up to the failure. Then resilience as I mentioned resilience comes from the rubber not from the filler. So if you fill the system at the first place you must have a understanding, that resilience will go down and hysteresis will go up. So this you must have a very clear conception clear perception many a times people think that, I am putting filler into the rubber system its strength increasing so the elasticity increase, "no" elasticity is contributing from the polymer rubber chains not from the filler. Filler is giving some sort of a point of you know immobilization as simple as it is this is the conception.

So again carbon black I am not going into the details of the carbon black, how it is manufacture there are definitely different methods of making carbon blacks. It can be thermal way it can be furnace way it can be made by channel is called channel black it can be made by lump black so different types of black. So what is important for you to understand at this stage size and structure as size structure and also the chemistry what is the chemistry as you as mentioned carbon black it can be graphitic it can be non graphitic, it can be graphitic means sp2 hybridize or it can have a defect sp3 hybridized. So what happen if you have this change over see obviously Graphitic type of a structure will give you increase in electrical conductivity, thermal conductivity but at the same time if you do not have a defect there it has less number of available functional groups. So it will not give you that amount of you know reinforcement for sure.

So let us try to concentrate on furnace black which are very commonly use, of course in this list there are two types of at least thermal blacks are also given which is all together a different ball game. But let us try to understand from the furnace black point of view. See SIF, ISF, HAF those are you know abbreviation, super abrasion furnace, intermediate super abrasion furnace, high abrasion furnace, fine furnace, fast extrusion furnace, this name N is the normal cure and S is the slow cure. So whether it has a influence on curing or not, Number 1 means 10 nanometer is the primary particle size second number 20 whatever is the second number after that signifies the structure. So as you can see super abrasion furnace is actually nanometer size it is 11 to 19 nanometer.

So up to this I will draw a line as I define so after this possibly possibly, this has this goes to the semi reinforcing category because the size goes more than 50 nanometer then on. So another thing is a structure while carbon blacks are formed in a furnace process. So that time so it is nucleating different particles this particle can have a sintered structure like a like a grape bunch of grape individual grape you consider as a primary particle but it exists as a bunch of grape and that is the aggregated structure. Now if you have aggregated structure it is easy to mix easy to incorporate inside the, you know rubber matrix but also as a individual particle it does not exist. So anyway so these are the different types of things and depending on so smaller the size, say for example, Aero tire you have to use some super abrasion furnace to have a optimum reinforcement which is 11 to 19 but that you do not have to do it for a truck tire say for example, you will be simply doing it with the ISF and half.

If you go to cycle tire you do not need that reinforcement you can go down to SRF for example. So as I must mention you as you have to make smaller and smaller particle with the fine control over the structure you end up putting more cost. So in cycle tire obviously why do you use you do not need it. that much of load is not going to be, that much of abrasion with the surface it does not leak well at all. So this is the primary particle size and these are the kind of you know structure.

See this structure is obviously higher than this structure this has does not have any structure. So low structure high structure you can see it from their primary particle with respect to that. This is a kind of a secondary structure you can say. So what is important five different important parameters particle size take it here, structure just now I explain and now we try to consider within a given you know filler. there can be porosity it can be mesopores some sort of a pores there inside a sphere this porosity, surface chemistry what sort of a functional as I mentioned it to you some sp3 structure.

So sp3 means graphite breaks and giving rise to some sort of a partial oxidation OH, lactam, CO type of a group and in fact all these thermal blacks are base modified. So you can understand sulfur cross linking is a base mediated reaction, I mean basic base catalyzed reaction and of course the physical form of it. So these are the primary parameters when you have to consider the reinforcement. So essentially if you look it at a carbon for the physical surface energy point of view of a carbonaceous particle it has four different sides. Of course you have a graphite structure strongly one is diamond type of a structure and some sort of a intermediate structure like slit.

If you have a slit type of a structure that is high energy high energy structure and that is very vulnerable easily can form a bond with the rubber matrix because there you can minimize the steel you have a chance to minimize the energy. Now coming from switch let us quickly switch another reinforcing filler which is silica. So silica also in its surface has three different functional groups available. It can be isolated the silicon OH it can be I mean two consecutive silica say one and two they have a weight it can be vicinal and it can be within a one one two OH group which is called geminal. Out of this three function and of course some bunch of Si-O-Si sort of a link, these are the four different chemically distinct sites available in silica.

Now the isolated Si-OH group is more active therefore although it doesn't react directly to the polymer carbon-carbon chain but if you use a coupling agent that can always very easily react with the coupling agent and therefore forming a bridge with the polymer chain. See unlike in carbon which can readily form a bond with the filler silica cannot do that job. You need to have an external agent which is called coupling agent that in one hand binds OH functional group isolated OH functional group of silica and other functional group of the. It is a kind of a two hands that is what the coupling agent, I will elaborate in the next classes what is coupling agent. See the silica is made by two ways one is called precipitated silica, another is a fumed silica of course there is a intermediate grade which is actually normally larger in size, which is called round silica not used for the reinforcement purpose.

It is a non-reinforcing category but quickly have a look fumed silica which is made by high temperature from $SiCl_4$ by decomposition of $SiCl_4$ and precipitated silica which is made from silicate sodium silicates and then acidification and then precipitate. So all those height wise you can come very close but from the original I mean from origin how it is made they are grossly different. Say for example isolated SiOH content that determines how much reinforcing my things can be, with the coupling agent aid of the coupling agent. So that is much higher in precipitated silica that too for the highly dispersible silica there is another category of precipitated silica. On the contrary in fumed silica you have a less content fumed silica, Since it is made at elevated temperature prepared it has less moisture content precipitated silica has a large.

So that way they are technically different but both of them in a NUT cell can act as a reinforcing filler. As you can see fumed silica typically this is the surface area. Surface area by the way is another character that defines the area available to form a bond and then you can see there they are more or less comparable but moisture content wise they are grossly different and what is not written here is the SiOH content. So this is what both of them are parallelly used but for different purposes. So obviously if you consider fumed silica and precipitated silica try to do a quick test on that.

This is a another test I must get you familiar with it is a strain amplitude variation amplitude sweep basically. So what it does at a very low amplitude you just try to do the switch from a small amplitude large amplitude even high amplitude. What happen this fillers they have a two different tendencies one part of it reinforcing filler, it must form a bond with the polymer chain. If not they will try to self aggregate. So if they self aggregate within this small amplitude this structure breaks down.

So more the reinforcing filler more is the size surface area they will try to aggregate basically. And from this test the effect is called payne effect from there you will be able to determine, how much the fillers are dispersed basically and how much is the reinforcement effect you see end of the day. So that is a gross you know manifestation of it that is how you can from here say for example blue one is obviously showing that you know precipitated silica where it breaks okay fume silica where it breaks is grossly different. So I am not going into the details but nonetheless hope it gives you.

you know gross simplification of it how you understand. So payne effect is a kind of a first test to understand the filler dispersion in a rubber matrix. So what you want actually the filler should not aggregate so filler filler interaction or breakdown should be nominal here. So if it is nominal then only you will be able to that means with a strain that drop, so it has a plateau value here and then it drops at higher strain and this change delta, modulus actually signifies a filler filler interaction which is not desirable you do not want it in your sample. So if you try to consider once I fill the sample how the modulus develops with a filler. The first thing is the polymer itself has a strength and that comes from the polymer network structure.

Second once you make put a dispersion think about a suspension in a liquid things are suspended then that hydrodynamic effects will add so it will build from here to here. Then in rubber structure with the filler with the rubber filler interaction. you get some additional thing and that is the point I talked about the reinforcement and that extra one comes from the filler filler interaction. And at a small amplitude what you destroy actually filler filler interaction and try to see how much actually is existing in your system. So this is what I am not going into that at a large stain of course it will break down.

So payne effect displayed as a reduction in modulus with increasing strength, for different grades of carbon black obviously at a given loading higher the reinforcing capability they will have a gross tendency to aggregates. So from there you will be able to discriminate say for example here 220, with the structure the effect 234 and 330 you see the payne effects are really different. 330 all together a different size scale so initial modulus were somewhere here but if you try to see in 234 which has a higher structure so it had little bit more, you know depletion of it compared to that of the later case. So I am not going into the details all together different subject but nonetheless, there is another effect is called Mullin's effect. What is Mullin's effect? See it is related to first one was payne effect was related to filler filler aggregate formation.

Mullin's effect other part the reinforcement it is about grossly about the rubber and filler interaction and it breaks actually at higher strength. You might have noticed it if you go to a grocery shop the elastic bands what they do they try to put in water and try to do 3-4 times and then they only form the pump band. So while forming there are different filler surface with that rubber forms, some sort of a bond in a non equilibrated way. So unless this is done by a slipping mechanism with the 4-5 cycle that's what in a testing module also, there are standard conditional modes where you do it 6 cyclical deformation then you try to test it for. So this is represents the Mullin's effect it is all together Mullin's effect is a subject of his own.

So if you try to see it from the hysteresis point of view try to do it from the different, you know constitutive modeling point of view Mullin's effect plays very very important role. And there are certain non-reinforcing filler categorized like calcium carbonate and also I am not going into the details kaolin clay it is basically silicates. These are also non-reinforcing filler and hard clay and soft clay, this is hard and soft I mentioned one is fine another is coarse. So quickly into other than that is particulate filler carbonate silicate, silica. you have other variety of reinforcing system which is in the form of a you know cylindrical aspects say fibers L by D ratio fiber by definition L by D ratio should be more than 100.

So it can be even more nanotube cases even further more. So more it is more is going to be the reinforcement as I said. So it can be in the form of a glass fiber it can be aramid fiber or in rubber, actually aramid fiber as such is not used in a modified form easily dispersible form it is used. Carbon fiber in plastics also it is grossly used and also the nylon fiber, which is has lot of you know this we are talking about a chopped fiber, not a continuous fiber by the way. So a short fiber less than 1 millimeter long fiber is more than 1 millimeter length.

When you come to non-nano obviously it is in the form of nano. So you have a whole gamut of carbonaceous nanomaterials here. It can be like a fullerene buckyball it can be in the form of you know nanotube, it can be again single ball multi-wall it can be in the form of a graphene these days very popular and it can be of course graphite is a very traditional material. So also you have a different varieties nano-cellulose this is getting more momentum because it is degradable sustainable. So some days are not that far when nano-cellulose will be one of the major filler in the rubber system. But on top of that there are certain clay system like bentonite based seranite based systems which can be having a platelet size of the tune of nanometer and those are used as a nanofillers as well.

So I am not going into the details from this point of view. But nonetheless quickly to wrap up in addition to that I as I said we have to eat puffed rice, you cannot have 1 kg of puffed rice eaten you must have some water without water you would be able to swallow puffed rice. So filler if you try to add more you must put some oil, for rubber water is oil always remember. So that is how you try to do it it will save the energy while processing, it will incorporation will be easier. So there are 3 different varieties based on the structure of course they are combination they can be olefinic that means CH2CH2CH2 type of a structure they can be the naphthonic that means they have a cyclical structure but not exactly aromatic and they have a aromatic structure so oil grossly helps this to achieve of it. So obviously the polarity will be more for the aromatic one then followed by naphthonic, then paraffinic.

Now the point is that when you try pick choosing for a definite rubber system, you must have to match with one parameter which is called solubility parameter. Say for example in EPDM you know paraffin oil goes well for you know natural rubber or SBR you know your naphthonic goes better and if you try to have a more polar system like say NBR your aromatic goes better. See there are there are 2 things plasticizer and softners, plasticizer is technically speaking, if it is a liquid system that gives you to the rubber that should depress the Tg, decrease the Tg. Softners may not be same, softners it may so happen it can create some sort of a lubricant on the surface so that it softens the whole mass, intermolecular forces to some extent it plays with that. But plasticizer technically following Fox equation, it should reduce the you know Tg of your polymer basically PVC, DOP is the classic example.

So if you just put DOP in PVC it becomes flexible PVC otherwise it is a hard or rigid PVC. So obviously there are some other plasticizers which is phthalate based, phthalates are sometimes dangerous I mean from the green sustainability point of view, maybe phosphorus based, vegetable oil based systems are also used. Tackifiers which improves tacks, see for natural rubber you do not have to bother about it has enough tack. Tack is actually used you make part by part component by component then you have to assemble so unless you have a tack there will be air pockets so you have a defect. But for the case of SBR or very synthetic rubber tack is really low so externally additionally, you have to add some you know ingredients like for example CI resin so that will improve its tack properties.

So CI resin is a classic example it can be a phenolic resin it can be rosin, hydrocarbon resins and tarpine base resinous mass. So overview process aids it can be chemical plasticizers I will talk about well, talking about because particularly natural rubber you get to have a very high viscosity. So once you process it, it'll not be processed unless in a controlled way reduce the molecular weight of it, and that is what the you know peptizer is used which is called chemical plasticizer. You can use lubricant so there are different purpose where the small molecular or oil small molecules are used with different you know aims and goals basically. So detail list is there I am not going into the detail teaching you rubber technology.

I do not have the intention but always try to remember this can often act as you know rheology 8. What is rheology 8? It will ease out the flow number 1 number 2 it will reduce the die swelling. So just try to understand from that point of view at this stage. So that is it I will not go to a details of compounding but within 2 or 3 lectures, I would like to get you familiar with the rubber compounding backbone to a non rubber people that is what my intention is that. So these are the some of the books I have given particularly if you try to understand rubber.

So practically plastic material put it aside at least at least the rubber technology Maurice morton and blow Hepburn and vanderbilt. These are the books where you can understand the rubber compounding in details. With that let us quickly conclude I talked about the filler reinforcing, semi reinforcing, and non-reinforcing and its origin based on the size, based on the structure, Means L by D ratio means safe and chemical functionalities it has black, non black, reinforcing and fibers I briefly covered about the fiber Fillers although I did not go into the details obviously. If your fiber length increases what happen? It will try to restrict flow more than that.

So classic example is that I do not know how many of you are from village. See the some of the houses are made out of the mud. In that mud intentionally the people use straw and that straw they chop it. So what is the intention? If you make it a long strand of straw what will happen you wouldn't be able to make that wall. Small strand with the clay it has the flow properties but still it will not fall apart because it will give you reinforcement.

That is the basics and then process aids, plasticizers are tackifiers. Next lecture to come as I mentioned carbonaceous material you have already favorable functionality in many cases, you do not have a favorable functionality. So in those cases you must do some sort of a surface functionalization in order to tailor and manipulate the property you want. Whether you want to see physical property improvement or you want to see in the rheological property improvement or in the longevity of it. So we will try to keep your finger cross for the next lecture we will try to see the surface state better. With that thank you very much.