Rheology and Processing of Paints, Plastic and Elastomer based Composites
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Lecture 28 : Rhelogy of Elastomers

Welcome to NPTEL online certification courses on Rheology and processing of paints, plastic, and elastomer-based composite. Today we are in week 5 lecture number 5.4 entitled Rheology of Elastomers. So concepts today covered will be very pinpointed. It is on Rheology of filled system and in comparison with the unfilled system as well. So you understand the what is the effect of filler into the elastomer.

So that is what we will often practice in manufacturing. So we will start with the without any keyword we will go into this. One of the composition will I like to show you and this is borrowed from this literature, One of the literature. So it is a kind of a side wall formulation basically.

So you can see it has SBR and you know polybutadiene at a fixed ratio. The all that they have varied is a in one case they added ATP or silica another case similar to, considering the surface area effect they have used the equivalent amount of carbon black. And additionally what you have the silane coupling agent in case of silica and that typically it is less than 10 percent with respect to silica volume fraction I mean typically 10 percent or 20 percent sometimes they use it because 30 is your silane coupling agent, close to you know 20 percent silane they have used. Here they used Si 266 one of the variant. And DPG is often used although today it is banned it is DPG is used, because silane coupling is a base catalyzed reaction and DPG is found to be best.

Today although people do it with the amine like X-L amine system but that is not as efficient as you know DPG is. So DPG is not fully replaced that way. So the best thing we realize how much, or how good is the dispersion is just first to have a you know strain sweep. So in the strain sweep as you can see the carbon-based compositions. So of course one thing before I forget they use two types of butadiene.

In one case is a you know straight change linear chain butadiene and other case they have used the branch one to have a parity what is the effect of the branching. But nonetheless here as you can see from both the cases, you see the storage modulus which is you know green and blue, you can see for the this particular part for the carbon shows a higher modulus here of course. And kind of breakdown you can see for both the cases are quite different. So here you see, there is a delta g change I mean as you can plateau to this thing you get it. And similarly from here you can see so both the cases not much of a aggregation you can see event of it.

And of course silica is lower in modulus compared to that of carbon at least that is reflected here. So kind of a rheological test you do it I will not say the rheological test as such, Here all this thing they are trying to do is, you know sweep test of the vulcanized sample strain sweep, frequency sweep and temperature sweep. These are the three modes actually of when you practice the DMA. So one of the things for tire application point of view is the just to assess roughly how good or bad it is going to be the reinforcement and as well what is the effect of the filler on the performance of the you know of tire compound. Say, for example, rolling resistance,a fuel economy point of view, and, wet reaction from the safety point of view.

So here you can see that from the temperature sweep, you can see the glass transition temperatures are little different for silica and again carbon black field system. Even that again amounts to the kind of interaction you have between the filler and polymer. So that will be little bit indication you will get it from there, but I am not going into the details of it, but all these measurements have been done in tension mode, Vulcanized rubber sample in DMA always advisable to do it in the tension mode, unlike on crosslink system you always prefer a shear mode of analysis. So the about the performance properties that quickly try to see at 0 degree centigrade temperature what is the tan delta. So tan delta as you can see is higher for both the silica-based system although you know branch to you know linear there is a very little difference, but you can you know infer from here that obviously silica field system is giving you higher, you know tan delta and that amounts to better wet traction or safety of it.

On the contrary if you look it at the tan delta values for carbon vis a vis silica field system, silica field system is always lower in tan delta at 70^0C and that gives you less rolling loss basically. So that is quite reflective once again I will point it out that, with the idea they try to see what is the amount of difference, they see branch polybutadiene bias bias with the linear polybutadiene they hardly got any of the difference here. Let us switch our attention to another system is NBR-based system with the 40 PHR semi-reinforcing N550 field system. Say they have done it with the capillary rheology, capillary rheology again for your easy recapitulation. It is done for the little bit higher shear rate regimes like at least starting from 10 second inverse onwards.

So there you can see what they have done in this experiment L by D ratio, they have varied and with the L by D ratio variation, they try to do the experiment at different shear rates. And here you can see this is the plunger pressure, can you recall? plunger pressure amounts the shear rate ultimately is related to pressure drop in the system. And with that at different shear rate you see the viscosity you can get it at different L by D ratio. So why L by D ratio is giving you the differences, one of the primary reason is entrance factor pressure drop or corresponding L by D ratio that I elucidated earlier. So that gives you that kind of a difference.

So entrance as well as exit part, if you have a high L by D ratio you do not have those. So after a certain L by D ratio if you start doing the experiments, the data will try to not much of a difference you will see. So similarly in other extremities they have tried to show you I mean once again there are two references we have consulted here. In another case a simple natural rubber filled with carbon black at that particular N 326 have with the high structure variety high abrasion furnace happens. They have used it from 10, 20 and 30 phr and of course compared with the gum.

See if you see a plot shear viscosity as a function of shear stress, what you can see it gives you a kind of a plateau behavior for the gum. Of course at a very high shear stress it thins it becomes low in viscosity. But on the contrary as you keep filling the samples it shows you all together a different behavior, it has no link to this one. And intermediate as a very small filled system, it was close to the gum but rheologically there whole lot different particularly 20 and you know 30 phr unloaded particulate higher it is most cheaper the material is going to become as you can understand more than reinforcement more immobilization more resistance to flow. But of course so if you look it at the other part of it which is extruded swell or die swell as a function of shear stress you can see that shear rate also.

So you see well that extruded swell was quite high initially and eventually at the highest filled system, it reduces quite long. So highly filled system means elastic contribution, elastic nature will try to get reduced. So it'll not give you large first normal force difference therefore it'll not give you that much of die swell. So what you can expect from here from this rheological signatures the filled system, including that 40 phr and 60 phr filled system the surface is going to be much smoother because the second normal force difference and its die swell is going to be quite you know diminished for sure. So that is that is what at the first plate you can look it at of course reinforcing to die and fill it is going to be different if you compare half vice a vice with that of you know N550 as I mentioned N550 being a larger size its immobilization of the polymer chains will be quite less contact with the filler will be quite less many a times it acts as a bearing effect rolling effect.

So therefore the die swell reduces. So that is how it works basically. So another thing let us try to look it at the gum we see you have A B C D from here to here and what is the difference the same difference the same source high curve is being taken same company and then you see it is 35 78 81 85 gradually we increase the money viscosity which is related to molecular as you can recall and that if I do die swell as a function of shear rate very very small mooney value 1 that is 35 1 you see it shows you all together different behavior than rest. The reason is that first one is more like a plastic material it shows you the melt fracture here at higher shear rate and that is quite common with a low molecular weight you know polymers raw materials. So once again you can always refer to there that publication I am just going to show you that how it works of course the experiment was carried out with the L by D ratio of you know 5 using a capillary meter and shear rate dependent of die swell 125 degree centigrade experiment was carried out.

So similarly if you load it with is a field system you load it with n 550 just now we are taught which is FEF and then you see the die swell value is going to be quite quite different for all these three polymers into the system at different different shear rate. So that way you can you can show that how die swell is essentially diminishing from system to system. So this is how you can very quickly have a check in terms of you know rheological properties how it is differing. So in a nutshell what I can tell you from here once again see filler molecular weight also makes the flow ability different die swell characteristics different on top of that when you load it with the filler depending on of course the filler size its surface chemistry it kind of a reinforcement effect it is going to be reflected not only in the viscosity but also in the normal force difference port first and second normal force differences. So rheological sense it may be in one case you find that you or if you have a master curve it was fitting well as a gum in the power law fluid regime but once you add on filler it you may have to invoke other models say carreau yasoda model or other model or or eiring model or other model depending on the complexity of your system.

So that is how is a bottom line so its filler alters the characteristic rheological properties once I try to look it at the entire regime of shear rate very low to high it changes its normal force characteristics that means elastic nature of it once again filling a polymer with a particular filler will try to reduce the elastic norm of it elastic norm once again is the recovery you are extruding it goes through and through the capillary gets elongated and then it will try to snap back giving you. So this particular things depends on the elastic strain and that elastic strain is reduced practically quite a bit in a filled system compared to the unfilled system that you have to keep it in mind. See once again as I told you see zero shear viscosity this particular experiment is being done at a in oscillatory mode again you refer to this highlighted underlined references where from you have taken it the cartridge to them. Since the viscosity is a function of frequency here oscillatory geometry you are doing. So in that case what we varied essentially a low molecular to high molecular weight systematically.

So as you can see from first to last initially obviously zero shear viscosity was less for the low molecular weight one that amounts to the molecular weight. So zero shear viscosity is proportional may not be directly in this case to the power 3.4 for the molecular weight of it. So that is reflective so gradually we see a increase. So it is not only that increases because of the effect so the very initial part low frequency part is whole lot different for system to system.

So that gives you a kind of a hold on so molecular properties of it. So it is a TTS is being done actually it is a extended frequency term using WLF equation. So the high frequency behavior slope is minus 1 is independent of the molecular weight. So one regime after a while you see since chemical characteristics is same all SBR molecules high frequency behavior is same but as far as lower Newtonian plateau is concerned is whole lot different. So similar so you can use directly the rheological means I was talking about the branching I was talking about the earlier the gel content.

All this change in you know molecular structure of the base elastomer can be captured using the rheometry and same is actually reflected in the flow and same is reflected in the finished product accordingly that you have to keep it in mind. So at a first place if you have three different polymer quickly run your rheometric experiment apply TTS and then try to have a master curve and try to look through frequency to frequency wise. And of course one thing which is not shown here you can always if you do it in a steady state rheology manner you can see look it through the you know normal force differences as I taught you in the very beginning. So that gives you about the you know what is going to be the in terms of the die well in terms of surface roughness of the extruded or finished products. So again in a you know oscillatory experiment or dynamic experiment you know crossover makes lot of sense.

So you can see two different types of polymer having a one is having a broad type of a molecular weight distribution and in other case you have a narrow type of a molecular weight distribution. So you can capture the crossover frequency crossover means G prime and G double prime process over. So viscous to elastic nominated response you capture. So higher crossover frequency for the lower molecular weight stops because they are more flowable ease of flow will be more. So is a lower molecular fragment of the of your distribution will be will matter much in terms of a flow.

So in general as far as extrusion is concerned to get a flow continuity broader molecular weight distribution is always preferred over the narrower distribution. So reason is that flow continuity. So you can see from those aspects so high and low crossover and that amounts to your you know type of molecular weight distribution you have and similar so you can anticipate what is going to happen for the branch polymers having more my branch I mean extended branching or short chain branching how it is going to affect. So here is a nano particulate form graphene is a very you know very small amount of graphene if you add it it changes the reinforcement properties electrical properties as well as your you know thermal and electrical conductivity quite a lot. So in this case they have used different composition with a silicon rubber.

Silicon rubber is very synthetic rubber and pristine form so you can very easily well discriminate the effect on rheology of the particulate. So they have systematically varies 0.5 1 2 2 different types of filler loading but in one case they have used coupling agent and another case they have not used they have used same DCP similar loading and try to cross link it after cross linking they have tried to do that you know oscillatory geometry on that. As you can see from here from pristine to the most filled one and coupled one you can see there is distinct difference in terms of you know composite viscosity as a function of frequency. And specially if I just discriminate here low to high frequency these differences trying to you know reduce basically.

So this kind of a studies you can often do it to foresee or to predict kind of dispersion you have kind of interaction the graphene or nano filler you have with the polymer matrix or kind of reinforcement you are getting. So those clues on top of that of course you can as I said you can do the capillary rheology also parallely and try to have a master curve and try understanding at low shear regimes how it happens if you want to do a compression molding how it is going to give you the finished or if you do injection molding how it is going to happen. That kind of analysis often you do and in this particular course I am not going into the injection molding other molding I will demonstrate you how you can predict extrusion extruded behavior basically extrusion is a quite common manufacturing process both for you know rubber and plastic industries. So here the same thing for SRGNS you can see how graphene nano sheets how it happens at a different temperature basically in terms of storage and loss modulus. So I am not going into the details you can look into the tan delta part of it and you can see how the tan delta obviously you can see from as you fill it more compared to the pristine one as your percentage volume fraction of the polymer reduces height of tan delta reduces.

But most importantly how much shift you are getting in tan delta I mean thumb rule is that if you have more interaction polymer filler interaction you know Tg is going to shift to a higher temperature. So that you have to look through how this kind of a shift happening and you have several models that that gives you a clue how good or bad the reinforcement is you can quantify the reinforcement that is another aspect of it I am not talking from the rheology point of view here at least. So clay is another useful filler at some point of time a lot of research has been done with specially the smectoid varieties of clay the common one I mean which you get it from nature is MMT, Montmorillonite and that has a stack of cut type of a structure. So here in people try to do in a dynamic mechanical analysis way this is the reference and they try to compare another relatively new nanofinner which is a cellulose nanofiber which is a sustainable filler. So as you can see a natural rubber pure natural rubber then once you add on the nano clay you get it a high higher plateau and even with the you know CNF which is you know cellulose nanofiber you get a larger plateau height.

So you can see this nanofiber as I mentioned it to you two things the geometrically one is the platelet type of a structure another is a fiber type of a structure those gives maximum reinforcement and since you know cellulose is more it has a more parity with the natural rubber structure obviously kind of reinforcement you get in case of you know nanofiber cellulose nanofiber is way higher and that raises the plateau modulus basically more and same is you can be reflective although I do not think you see a lot of difference in terms of tan delta for case to case but obviously height of tan delta whole lot difference. So for CNF case at equal loading level you see much reduction in the height of tan delta and that signifies that you have better amount of polymer filler interaction polymer filler not filler filler in case of you know CNF while the nano clay and NR the pristine one the control one hardly any difference they have merge on the same point. So nano clay in essence in this case at least does not show you much of signature of reinforcement as you compare it with the cellulose nanofiber. So that is how your analysis has to go there. So why I talked about here about the dynamic properties again I will clarify double clarify that dynamic properties and dynamic rheology hardly it is different it is your perception when you talk try to look your material from the solidus point of view at a lower temperature relatively you try to look it in the G prime and G double prime way.

Once you try to look your material for the fabrication try to look it in a fluid point of view how fluidity it has I try to do temperature experiment at a higher temperature and try to look for eta prime and eta double prime as simple as that. So from that point of view also your your experiment has to be so designed. So whatever you know properties you get it in bit higher temperature here that amounts to the rheological property until the point the things are not cross linked. Remember if you crosslink it you are permanently you know freezing the flow. So no question of fluidity and that point of time is better to look it at from the solid point of view represent it with G prime and G double prime rather than eta prime and eta double prime that is what your perspective should be.

So I will not stretch it further but hope I have given you enough clue about the fact that how how the pristine polymer vis-a-vis a filled system its characteristics changes. So again we will come back a little bit more into those two important aspects not only the shear stress as a function of shear rate matters. Power law or Eiring or or or you know carreau yasoda as a type of fluid it matters but also the die swell characteristics and surface finish which is die swell is related to the first normal force different surface finish is related to more of the second normal force difference how it matters for a filled system. I have actually practically useful rubber systems that we are going to highlight in the next lectures. With that thank you very much.