Rheology and Processing of Paints, Plastic and Elastomer based Composites
Prof. Santanu Chattopadhyay
Rubber Technology Centre
Indian Institute of Technology Kharagpur
Lecture 16
Rheology of paints 2

Welcome to NPTEL online certification courses on rheology and processing of paints, plastic and elastomer-based composites. Today we are in week 3, lecture number 4 which is titled as rheology of paints, lecture number 2 here in the same title. So, the concepts covered will be little bit again into the viscoelastic behavior how to capture, I mean there are certain types of coatings which are used which are UV curable. After application of it, it is cured with the UV light for the surface curing. So, optimizing the rheology of the coating that is the most important. Impact of particle loading on coating that is also important because you have lot of pigments in there.

So, its particle size affects the rheology whether the particle size distribution affects the rheology and how to quantify that. Impact of polydispersity of those particle size distribution on flow behavior. Further factors affecting coating rheology and let us take one case studies, one of the paints which is a very advanced paint and then we will take it forward for its development in terms of rheology and the rheology point of view. Once again the keywords I already talked about.

So, viscoelastic properties, it is not low it will be linear viscoelastic region LVR, it is a linear and then complex viscosity and zero shear viscosity, glass transition temperature I already talked about. This you always can refer to if you wish to read more on this. So, now let us try to understand UV curing once again. So, curing is a chemical reaction. So, if there is a chemical reaction during curing there will be exotherm.

So, what you monitor in this particular rheometric analysis three things together. One is G type prime and G other is G double prime which you get it as a standard output when you do a oscillatory measurement. At the same time you have a thermocouple probe just beside which measures the temperature you know in situ whether it is exothermic, endothermic etcetera etcetera. So, if you can see from this plot say G prime versus G double prime your red one is a G double prime. So, initially it was liquidus.

So, G double prime was dominating over the black G prime and it crosses over you see at some point of time see here it crosses over and then you see this sort of a behaviour. So, and finally, I mean black one crosses over the red actually. And you see that it is getting cured that process. So, G prime is greater than G double prime when G prime equals to G double prime that is the gel point. So, exactly here the cure is happening.

And in terms of curing since the curing is going on you get a temperature maximum which is slightly lagging here of course. And then is a time is a actually you are monitoring as a function of time here you have kept the shear rate as a shear strain constant which is 0.1 percent here in oscillatory measurements you got it from the LVR sweep you know amplitude sweep basically. And then omega you kept it Ted rad per second constant and apparently you did a isothermal measurements temperature was constant, but this blue temperature is the in-situ temperature is capturing in instantaneous generation of because once curing happen is exothermic reaction happens. So, you try to have a UV curable link here which is soft touched final G double prime should not cross 0.

1 MPa that is also another parameter here. It is a soft touch application on the coating you feel like it's a rubbery sort of a thing. So, in fact and indeed if you just go by the temperature process see end of this peak signifies the curing is over. So, that way simultaneously this kind of a rheometric in-situ rheometric experiment enables you the what time it takes for the UV curing. Of course, one thing I forgot to tell you here it is not a in-situ curing like it happens in rubber curing it is you have a UV lamp which is actually giving certain doses of radiation into the material per unit area.

So, that is the typical experiment you have to perform that in order to better understand the curing process. Curing behavior of powder coating again as I mentioned earlier, As I mentioned earlier, also here for your this thing two powder coating systems are taken coating one and you have a powder coating two one is given you the black color another is given with the red color both G prime and G double prime. Temperature is also in-situ monitored in this case you see both the cases temperature more or less follows in-situ temperature same order. Again these are the condition which are kept constant here and you see from this obviously the crossover and also the highest modulus or equilibrium modulus is whole lot different. Once again as I mentioned a soft touch or harder coating application point of view first curing activity, slow curing activity you have to take a call whether to go with the coating one or coating two.

But hope you have understand as a function of time this kind of a rheometric studies how important it is from the application point of view after you coat it how much temperature, how much time you have to wait for to curing to happen say. So, that is very very important. So, again as I mentioned one of the major constituent in the paints is pigment. So, it is a all solid content that matters how much solid content that paint is having there. So, in this case first case 40 percent coarse talc 29 percent you know here 0 percent here this is unfilled only the resin part of it.

Obviously, higher the filling higher will be the low shear viscosity of it. So, small particles will increase it further why? Smaller the particle more will be the surface area. And in terms of electrostatic forces as well as inter particle forces it will be much higher for the lower particle size. So, note that the viscosity is almost independent of particle size at higher shear rate. You see the plot B where viscosity is monitored as a function of shear rate and you see at the lower one 29 percent mean particle size of 5 micron here 19 micron here although they are drastically different here by separated by this much in terms of viscosity Pascal second and which actually almost levels up becomes equal or close to one another at a high shear rate.

So, that is also important there the hydrodynamic part is also only matters nothing more than that hydrodynamic part depends on the percentage of it 29 percent filled. So, they are going to reach almost equal level at high shear rate. So, that is one of the point. But most interestingly see impact of particle loading volume fraction of loading how rheologically it affects that you must understand. See if I just try to monitor zero shear viscosity or low shear viscosity as a function of volume fraction of particles you see this kind of a change of viscosity you can often see initially they not they very very less increment happens then suddenly after filling it drastically increases.

So, there are three regimes you can define here following Krieger or Dougherty relation where eta by eta 0 equals to 1 minus phi by phi m to the power some minus eta into phi m what is eta is intrinsic viscosity equal to 2.5 for the spheres and phi is the volume concentration of the particle and phi max is the maximum packing fraction. So, that way eta is the viscosity of the suspension eta 0 viscosity of the medium of the solvent or liquid over which it suspended. And if for a Newtonian behaviour you will expect if this phi-by-phi m factor is less than 0.1 if it is less than within the regime of 0.1 and 0.5 you grossly expect it will give me a shear thinning behaviour, but very interestingly if it is highly filled when phi by phi m is greater than 0.5 it will give you a shear thickening or dilating type of a behaviour that is how there is a very very sharp paradigm shift. Also in terms of the particle size distribution see you can have small to large particle fraction rate distribution or you have a almost like uniform or narrow distribution of the particle size that you can always do different measurement like you can do DLS light dynamic light scattering you can do you know electron microscope you way also you can determine particle size and distribution basically. So let us try to understand how it is going to affect the polydispersity. See if it is a 100 percent large particle you get a zero shear viscosity if it is 100 percent small particle size distribution you got to somewhere high viscosity following the Krieger-Dougherty relation once again.

$$\frac{\eta}{\eta_0}=\left(1-\frac{\phi}{\phi_m}\right)^{-[\eta]\phi_m}$$

But in between you can always play with if you wish to manipulate on the viscosity of your suspension you can play with the dispersion narrower wider. So that way if you want to increase the solid content of the sample keep the viscosity same then increase the particle size distribution that is the way you can manipulate you can engineer it that way. Conversely narrower particle size distribution will increase the viscosity as mentioned following the Krieger-Dougherty relationship and of course as I mentioned depending on the volume fraction you use you can make it to behave like a shear thinning or shear thickening type. That in terms of size only I am not talking about that you know some of the clay particles always gives a thickener like laponite as I mentioned bentonite varieties of clays that intentionally added to the suspension of paints and coatings. See there are other than your rheometry you can use different instruments like dynamic light scattering which gives you size distribution as well as zeta potential in the static force or surface you know charges it has whether there is a steady crowding or not.

You can do the microscopic technique you can do it is a spray particle analyzer technique or laser diffraction technique. So that way small size vis-a-vis large size or a distribution of the size or a volume fraction how it is going to affect the rheological property you can do two parallel experiments side by side and you come up with the quantification of it. So now let us try to quickly understand one application there are thousands number of types of paints available antifungal, anticorrosive etcetera etcetera. But let us try to take a state of the art today's application. Today alternate energy is a I mean hue and fry I mean to tap energy from alternate sources solar energy is one of its kind.

So what it demands environmental friendliness bio-compatible and renewable you know source of energy. In these aspects one particular type of coating is very important which is known as spectrally selective coating, temperature sensitive spectrally selective coating TSSS. So we would like to make here rheological try to establish that coating system with a POS based system. So what you want to do this particular POS increases the solar absorptivity so that you can tap more and more energy. So spectrally selective means capable of absorbing high amount of solar energy and emitting low amount of thermal energy back to the surrounding and this is what is called spectrally selective.

So POS treated and how the why POS is treated and how the property affects that the subject matter of the paper I am discussing here. So POS dispersion influences the rheological properties of the paints obviously as I mentioned any suspension will influence POS improves the solar absorptivity. Proper rheological properties are essential for uniform distribution of the coating and rheological properties could be used to predict the solar absorptivity of temperature sensitive spectral selective coating systems So let us try to see step by step. So due to their sensitivity to the thickness it is extremely difficult to prepare a uniform smooth and thin coating with a dense distribution otherwise our intention will be defeated. So in order to reduce the viscosity improve the problems rheological properties should be modified see black thickens the sensitivity spectrally selective paints at various PVC ratios.

PVC is the medium here resin medium here in this current context. The various POS dispersions were used for pigments treated in order to determine the influence of POS structure I mean POS can be various types of modified available. Liquid paints were prepared at various PVC ratios PVC to the POS ratios and the rheological properties were correlated with the solar absorptivity that is the essence of that particular paper I am referring here. So quickly three types of POS are used this is isobutyl trisilanol treated trisilanol isooctyl POS and trisilanol phenyl POS three different types of POS materials are used and after loading in the PVC, PVC the matrix the increased value of in stress usually illustrate the stable dispersion. So sedimentation part is well taken care of second but the high in stress could also lead to decrease in the ability to flow and leveling that I mentioned.

So you need to optimize high but how high it should be accordingly you have to pick choose a particular POS and its level and its level of loading the proper balance of property is therefore essential for a good quality of functionality I believe you understand here. Then again you see viscosity as a CRI you plot it for various various you know loading without any POS PVC to black loading you have done it then on top of that three different types of POS in A B C and D you try to see it that is the rheometric experimentation is performed in order to optimize our intention here. Again the oscillatory measurement shows you try to see the optimized level PVC to 11 weight percent or 32 weight percent they have optimized. So what is the conclusion after oscillatory experiment as oscillator is nothing but what you get as an output g prime g double prime versus omega which is the angular frequency of it always you can refer it to you know shear rate also. So for higher pigment loading g prime becomes predominant and elastic properties are main part of the contribution that is very obvious but once again how much dominance we want that you have to optimize from here.

Again the flow behavior you do rotational rheometry parallelly and see the different regimes 0.1 to 100 at least at this stage at the optimized level from taking it from there and using the power law equation although the earlier equation for the suspension would have been more relevant but nonetheless in this paper they have followed the power law equation and then try to see flow behavior index that means how shear thickening it is n value with the PVC loading for different-different POS system they have evaluated with the pigment treatment. So again the binder TSS paints with pigments without POS treatment TSS paints with IO, IO was the optimized one I show between one in terms of dynamic modulus and g prime they have tried to optimize here. I am not going into the quantitatively each probing into the data but I what my intention is to make you understand given a rheometer given a paint system you have to develop how you go about step by step how do you pick choose what I told you already over the master curve which one is optimized from your application point of view. So that is how as I mentioned you can do both ways you can make your paint try to analyze the rheological properties in terms of application or from the very beginning you try to make a rheological properties optimized first so that your developed material will perform accordingly so both way it is possible.

So I will not go further this was taken from one of the papers I will refer it and other than that my reference has remains all the way same excepting this surface coating science and technology by Swaraj paul you must try to have more and more knowledge about the paints and its applications. To quickly to conclude what I talked about the viscoelastic behavior for UV curing cured paint based system Optimizing rheology of the coatings, impact of particle loading particulate that was important krieger-dougherty type of equation I have shown you the viscosity, the packing fraction how it varies. And impact of particle loading you see depending on the maximum packing fraction where you are it can give you either Newtonian behavior it can give you you know in the shear thinning behavior and if your maximum packing you approach close to that it gives you shear thinning also. In fact, if you look at any rheological behavior of the ideal system solution, it shows you many a times like this see you have a upper Newtonian at a lower shear rate you have a shear thinning behavior and at the end not here you get a another Newtonian part, but in this case after this thickening you try to get it. So, this is a shear thickening behavior dominates.

So, obviously, I am trying to plot this viscosity as a function of shear rate. So, further I have shown you also with the case studies while I was talking about very advanced coating system which is a solar coating system spectrally selective and you know temperature sensitive the thickness matters basically that I have not highlighted. Depending on the viscosity it actually gives you idea of how much thick or thin your coating is going to be after application that is also taken care of I did not go into the details of it just wanted to give you how rotational viscometry how oscillatory viscometry you can take it in the course of development of such a kind of a advanced painting system. Hope you will be applying to your businesses and thanks a lot.