Rheology and Processing of Paints, Plastic and Elastomer based Composites
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Lecture 11
DMA -In-Light of rheology

Welcome to NPTEL online certification courses on Rheology and Processing of Paints, Plastic and Elastomer-based Composites. Today we are in week 2 and lecture number 5 and we will cover DMA in light of rheology. So, so far so forth I talked about the oscillatory rheology while talking about the parallel plate geometry and even when I talked about other curometer or cure meter or rheometer like ODR, MDR and RPA. So, in this context we would like to clarify what is the difference between the DMA and oscillatory rheology in general. The concepts covered will be viscoelasticity, little bit on resilience that means elastic and you know viscous component of it since you all know the polymer is a very viscoelastic material. So, that is very important understanding of it.

How does DMA work? Common geometries used in DMA responses to classical extremes and oscillatory test, storage modulus, loss modulus, tan delta, basic conception. A typical DMA plot, oscillatory test methods in general dynamically, measuring Tg of by DMA, effect of crosslinking by Tg and effect of temperature on viscoelasticity. Once again I will not go through each and everything, but some of the keywords you must borrow it from here so that you can really figure out the critical keywords and the conception involved there. The viscoelasticity and resilience, Voigt Kelvin Voigt sometimes is called model or Maxwell model, sinusoidal shear or tensile strain I mean LVR particularly linear viscoelastic regions, storage loss modulus, tan delta, damping constants, phase angles, complex elastic and viscous modulus, Hookean solid, Newtonian liquid, then a mechanical thermal analysis which is abbreviated as DMTA, phase transitions, crystallization, melting, glass transition temperature, gelation, curing and reaction kinetics.

Once again I mean as I talked about the viscoelasticity, polymers in general they always have two components, one is the elastic component and another is the viscous component. Now the essential difference between rheology and DMA classically is when I talk about rheology we try to see the terminal region of it that means we always refer it to higher temperature or lower frequency. So when I talk about the properties, the dynamic properties in general we will always refer it to comparatively lower temperature as well as high frequency aspects of it. So that is the basic difference between the rheology particularly oscillatory rheology and I mean dynamic mechanical properties. Otherwise DMA does not make I mean difference if you consider the whole regimes of it frequency and temperature window of it, it is all the way same, it means the same thing.

So a real polymeric material have viscoelasticity. See maybe when at a higher temperature viscous component is more, it is more of liquid than a solid. At lower temperature is more of solid, it is solid dominant and I mean it is a dormant when liquidity or fluidity is dormant there. So that is the basic difference in general. So when the load is applied to a polymeric material it is time dependent.

So we need to consider not only its strength but also extent to which inputted energy will be dissipated. So that dissipation if you consider at ambient condition it amounts to fluidity and that is the viscous component of it and one which can be recovered back once you withdraw the stress, you call it elastic in nature. So that is the general conception you must borrow it as a beginner. So the first way to look into the viscoelasticity have a very simplistic mechanical model. see spring is a absolutely hookiens solid where stress is proportional to strength and a dashpot is nothing but in a cylinder or you have a piston moving in a fluid medium.

So in that it follows Newton's law where shear stress is proportional to rate of shear and in that essence actually the time dependency comes into the picture and there is a viscous part of it. So once they are in a parallel combination as you can see it is called Maxwell model when I mean serial combination is Maxwell model and when they are in parallel combination you call it Kelvin-voigt or voigt model in general. So these two models actually are very good to depict the dynamic properties in general but if you look at transient properties like stress relaxation or creep, Maxwell body this is the Maxwell one, Maxwell model the first one is better for depicting stress relaxation which is a exponential behavior grossly it depicts. Whereas the other part of it that means Kelvin-voigt model it depicts creep in a better way not the stress relaxation. So in general if you just add on these two together that means four parameter model that grossly depicts both of the phenomena but in general dynamic properties are depicted well by both these models.

So again the dashpot represents the dissipated part that means it is actually amounts to the loss part or component of the modulus sometimes you call it or it is equivalent to eta dash and while the other part the stored energy part it represent E prime or storage modulus you call it sometimes and in viscosity notation it is eta double dash double prime that is the oscillatory sense it makes in that essence. So that way Maxwell model I am not going into the details you can always refer back to my earlier NPTEL course which was on characterization of polymer last semester it was offered you can always refer to that. Again dynamic testing you can do resilience. Resilience simply you can do you have a ball you drop it down from certain height it falls it collides with the you know your floor and that it actually recover some height. So this ratio of this height from the height it recovers divided by height from what it was fallen that gives you the storage component of the you know modulus basically and that is in turn in general known as resilience and that is a very resilient I mean rudimentary test you can always do and whichever unrecovered that is the loss part of it dissipation component of it.

But nonetheless it is tested in a more precise way by dynamic mechanical analysis and across a range of temperature and frequency you can test the same how much is the storage how much is the loss. Once again in modulus sense solidus sense which you call it storage in viscosity term that is the loss and vice versa. So it is represented as a complex number notation that means when I write the total modulus E or complex modulus you call it is going to be the one component which is storage and with I imaginary component which is dissipated. And similar so for the viscosity point of view complex viscosity is given as is the storage part of the viscosity which you really can see and it is actually minus sign come into eta double prime and this eta double prime is actually related to this is the cross relation it holds. So I am not going into the detail derivation you can easily derive how storage and loss this cross connections are connected by a factor of omega there is a angular velocity of the experiment or frequency of the experiment.

So let us try to understand little bit deeper into that. So in DMA or oscillatory measurement which are the parameters you can vary of course one is temperature another is frequency another is the strain. So how much is the dynamically you are deforming what is the amplitude of it. And another part very important to understand is LVR which is linear viscoelastic regime. So when you do stress you apply stress versus strain.

So it gives you this is the amplitude or strain I represent in general and this is the stress so it gives you linearity after that it deviates and this linear regime remember this when I talk about this strain I mean it is a dynamic strain. So this straight line relation when up to that stress is proportional to strain you call it linear viscoelastic regimes. But always always we do perform dynamic experiment more or less into the LVR region where your modulus is only function of time but if you cross it, it becomes a function of time as well as strain and that is what is called non-linear viscoelastic regimes. So you often do many a cases in the linear viscoelastic regimes most of the experiment for the simplicity of it. So this oscillatory mode of measurements has an amplitude and a frequency I s sin omega t and so stress versus strain always there will be lag and that lag basically represents the phase angle delta.

So if I plot a complex modulus I always get it two components of it they are separated by angle theta one is the storage component another is the loss component and that is what I write in a complex number notation. So that is the result of the modulus of it and if you represent the vector part of it. So how does DMA work? Consider a constant input and output function a sine wave the best way to realize either sine or cosine wave which as a periodic wave periodic deformation I mean you put stress in a periodic wave monitor strain and try to get the ratio of it that gives you the complex modulus of it as simple as it is. So the resultant sine wave then you try to have a two components of it out of it E prime and E double prime and the ratio E double prime by E prime is called tangent delta which is always refer to specific loss you multiply pi, pi tan delta is specific loss. So, if you look it at the anatomy of it generally DMA machine it grossly looks like this it has a LVDT part of it and then you have a temperature enclosure, force transducer, force motor and of course the heat sink heating and cooling system.

Tan d = E"/E'

Now I am not going into the details again I will refer this to the you know side given here and you can always refer to my earlier NPTEL courses where detailed depiction is given but nonetheless probably it makes sense to you what is E prime what is E double prime what is eta prime what is eta double prime. And again in rheological rheology reference I will always say when you measure it at a ambient or little bit out of ambient temperature regime and within that frequency regime you call it dynamic mechanical properties. So always refer to E prime and E double prime. When you do it at a higher temperature or low frequency extremely low frequency you call it oscillatory rheological properties. Instead of E prime and E double prime you try to represent eta prime and eta double prime that is the convention.

Otherwise DMA and you know oscillatory rheological data does not make much of a difference in that strict sense of it. Of course DMA you can do it in different modes so far so forth when I was talking about starting from rotational rheometer and then I talked about various types of you know for rubber specifically Muhly viscometer starting from there ODR I talked about MDR I talked about RPA I talked about parallel plate rheometer also. So you might have seen it is always in the shear mode I referred is a shear deformation. But when you practice DMA in general it is a solid material most of it from for the for the solidus point of view you can have different modes of it analysis. You can put it in a tension mode that means you elongate the material and on elongation you do the you know apply the periodic sinusoidal stress and try to monitor strain and that's what is called you know tension mode and it is good for vulcanized rubber say for example.

You have a film on the contrary either you go for single cantilever or dual cantilever mode. So what type of a film you have what is its stiffness. If you have a single cantilever beam then your whatever error comes from the one point where the film is hold here you can see here it is doing to and fro motion here or else your film is very weak you try to do a dual cantilever mode basically. So you put it from the both ends fix it there and try to deform from the middle part of it. And similar so you can do it in the compression you can do it bending, but shear you can see shear is pretty well used in most of the oscillatory rheological modes basically.

But when you are of course bothered about the extensional viscosity extensional part of it you can always go for the tension mode of other modes of analysis. So I am not going into the details of it again I will refer it back to the my previous NPTEL courses where a detailed depiction on various modes various type of DMA measurements is given very very in a detailed manner. Once again either stress or strain see if you take its stress I am putting a tensile notation you can always refer to a shear notation also. And similarly you can see this is the stress try to see what is the strain response of it either again epsilon or gamma it depends what mode generally sigma refers to tension you know epsilon refers to tension whereas tau and gamma refers to shear mode of analysis that is the convention in general. Now we can see first one is stress second one is strain and there will be lag and that lag is delta what I talked about phase lag phase gap there is a phasor diagram I showed you and therefore what you are evaluating ultimately you know three component of it E prime E double prime and tan delta that means delta, tangent delta is the usual representation of it.

And that you are trying to measure across various temperature various you know frequency and various of course you can measure at various time also that is also a special case particularly thermosetting curing regime you can do that deformation and try to see with the deformation during curing how much is the effect on viscosity will be abruptly shooting high actually that also you can monitor it depends on the perspective of your analysis all together. So as you can see for a purely elastic material phase lag between stress and strain will be 0 which is purely viscous and Newtonian fluid is going to be 90 degree. So sin function you are applying you are getting output as a cosine function. So always viscous elastic fluid will give you in between 0 to 90 degree phase lag. So delta is either in between 0 to 90 degree for a viscous elastic field here.

So if it is more elastic that means it will be close to 0 that is what you get it at lower temperature and higher temperature will be close to 90 that means it is elastic dominance that is what I meant. So I hope that conception is by now clear to you the phase lag here see there is no lag and you see 90 degree out of phase. So oscillatory testing you always try to measure delta and monitoring delta where it is exactly located close to 0 or close to 90 you will be able to say what is your character of the material whether it is close to elastic whether it is elastoviscous or viscoelastic what is dominant hope it makes sense to you up to this. Again I do not have to define but for your again those who are taking up dynamic properties as a beginner modulus is stress by strain, storage modulus is stress by strain into cos delta and loss modulus is stress by strain into sin delta that means out of phase of it and tangent delta is basically ratio of these two modulus. And similarly you can write it in viscosity terms also only thing is that correspondingly you have to take it eta prime eta double prime by eta I mean eta prime by eta double prime you have to take it into account that is the tan delta basically.

So this is what it is I am not going to elaborate so this is the phase diagram I mean phases diagram this is the loss component of it which is the if I write a complex notation if this is the modulus then this is your storage and there is I E double prime and this is your delta makes sense. Now if I plot it again this loss modulus and storage modulus as a function of either temperature or time and frequency or time is inverse of frequency. So whatever you get it in you know modulus versus time exactly it will be opposite to that. So you see for a generally amorphous polymeric material like rubber you see glass state it will go through a glass transition and then you have a rubbery plateau and then you have the liquid type of behaviour it is showing. So that is what that master curve looks like with the temperature it follows time it follows but with frequency it is going to be reversed so it will just opposite to that.

So if it is a frequency representation it is going to be something like this. So what I meant this is called terminal region this is the boundary and over which if you measure anything that I will refer to oscillatory rheological properties anything across this boundary left to that I will call it dynamic mechanical properties that is the demarcation thin line of demarcation. So once again you can for a master curve you can define your zone at a very low temperature or high frequency it is all glassy zone. Then there is a transition zone where rubber transforms from glassy state or polymer transform from glassy state to rubbery we were both are solid though. Then if you heat it up further it goes through a terminal region that means it starts flowing basically.

So you can grossly see manifestation of at least if not more you know four distinctive regions basically of course for a nano composite it gives you a weird behaviour you see another plateau and then before it falls. So that is called terminal plateau. So I am not going into that complication right at this stage but nonetheless probably it gives you a gross understanding of a master curve this type of a curve across a wide range of temperature or frequency you call it the master curve. Once again I will refer you back to here this pdf document you can refer to append it here or else please refer to my earlier NPTEL videos on you know. So as I said oscillatory test or dynamic test which you call grossly you can do amplitude sweep that means you are keeping temperature frequency time constant only variable is modulus loss of storage as a function of amplitude.

Then there is a frequency sweep you put rest of the parameter constant keep amplitude constant keep temperature and time constant and go for a change of frequency. Then time test and temperature these are the four major modes of analysis I mean types of analysis you can do keeping one one parameter out of four parameter like amplitude frequency time and temperature and rest one of them you are allowed to vary. So you try to understand the gross you know viscoelastic behaviour across those parameters. So when you look glass transitions from DMA sometimes it is more sensitive than standard DSC of course you have a MDSC more precise DSC that will give you of course when you refer to absolute determination of glass transition temperature you know dilatometry is the best technique rather than neither DSC nor DMA actually. So it can detect secondary transitions also that you may miss it out in you know DSC and measurement of mechanical response and many clamp types for various shapes and sizes.

So you know dynamic properties are highly highly geometry dependent. So you have to pick choose as I mentioned what type of a geometry clamping geometry of a choose for that also depends on the initial modulus and geometry of the specimen you are handling with. See why do I do amplitude sweep as I mentioned if you simply plot modulus storage modulus of course I am referring here with the amplitude. So A sin omega t I am putting A or you can put it like say sometimes strain. See I am referring to epsilon equals to epsilon 0 sin omega t this epsilon I am varying in terms of strain and then as I mentioned it you can get so suppose if in place you know storage modulus I put stress directly storage component part of it I get to see any linearity then non-linearity I will determine this is the LVR this region from here to here because it is linear.

Now where what amplitude I should pick choose for the rest of the sweep test the frequency or temperature I ideally should somewhere in between. So problem is that if I do frequency sweep if I choose this point because this is giving me the ultimate after that it undergoes there are chances during the experiment it can over suit it can go from linear to non-linear. Here remember here is a modulus is only function of time and here modulus is a function of I am putting in a static sense not prime or double prime its temperature and deformation that is the problem that is the difference and that demarcation as you keep filling the polymer your linear risk elastic region gets shortened and shortened and shortened. And you know in addition to that while varying the amplitude particularly for a filled polymer you can probe into a effect called payne effect which actually amounts to filler filler aggregation that you can discriminate. So structural strength rigidity changes dynamic yield point those can be captured using amplitude sweep.

Frequency sweep you can do I am not going into details that gives you gross idea about the molecular weight molecular distribution degree of cross linking stability impact resistance that is kind of a indirect you know indication you can get it. So you can often look at the crossover between E prime E double prime that amounts to sometimes gelation gel point gel to salt transition. So those are very very important for the salt to gel transition that kind of a transition. Time sweep particularly for the thermosetting agents thermosetting polymers you can often capture the gelation curing degradation. Similarly temperature sweep gives you a gross idea about curing gross idea about the change of variation I mean variation in properties as a function of you know temperature and that is very very important for engineering application point of view.

In addition to that phase transition crystallization melting those you can capture again I am not going into the details of it right at this stage because it is not that relevant which is more relevant understanding the difference between you know dynamic mechanical properties what information you get it and rheological properties what you get in. The rheology part I already elaborated in earlier you know sections. So where to pick this is for your information giving but it does not have much of significance from the point of view of you know rheological context but of course so which point you have to peak choose E prime change of E prime change of E double prime tan delta peak which one is close to the particular given transition that is also elaborated in my earlier NPTEL I am not going into the details of it right at this stage. And of course when it goes to a glass transition in tan delta terms you get a peak there you get a peak for storage loss modulus also and storage on the contrary give a point of inflection. So where to peak choose where to peak choose as a gas transition temperature is debatable basically but nonetheless is all depends on the perspective.

This elaborates about particularly for the blend system immiscible blend system. So what should be the immiscible blend system what should be the Tg like using Fox equation you will be able to predict basically and whether it is a compatible or non-compatible if it is immiscible blend system you have a single Tg immiscible you have two TG's that kind of a monitoring often you can do it using DMA. Cross linking again if it cross links then accordingly you will be getting the changes in terms of this properties like E prime E double prime and tan delta. Generally as the density of the sample increases molecular motion in the sample is restricted causing a rise in the in a glass transition temperature and for low values of cross link density Tg can be found to increase linearity with the number of cross links and high cross link density. higher the cross link density that Tg is broader.

$$\frac{1}{T_g} = \frac{w_1}{T_{g1}} + \frac{w_2}{T_{g2}}$$

And I mean there are still some ambiguities I am not going into the details but in general if you see this is a uncross link master curve of a uncross link polymer as you keep on putting the cross link this modulus increases and generally if it is highly cross link you will not be able to see much of the changes as if TG will be masked. So these are some of the things which you often you will be interested looking at but nonetheless. Once again I will re-emphasize dynamic mechanical properties or oscillatory rheology will always give you a gross picture how much it is elastic how much is to discuss that behavior you will be able to capture and that has lot of implication not only for the application or property point of view but also in the fabrication. If elastic property is dominant once you extrude a material cell it is going to swell up more die swell is going to be more you do not get a smooth surface the reason is a once again because of the normal force differences as your material is most solidus higher will be the first normal force difference second normal force difference. So it will be reflected in terms of you know die swell or calendar shrinkage as well as the surface irregularity or surface roughness.

So that is most important capturing the elastic vice versa viscous response of it. I will not elaborate much on this DMA because DMA is not the context here understanding the gross difference between the oscillatory rheology vice versa the dynamic mechanical properties is more important in this particular lecture. In terms of the books you always refer to some of the books which I already have given of course the applied rheology one of the this thing is by Anton Parr their publication is really really good. Actually they have themselves as their publication. So what I will conclude from here is what I defined here the essence of viscoelasticity and resilience its conception point of view what is storage what is loss.

Then how DMA works I did not go into the basic principle neither I explained very much into the you know in the principle of that equipment or anatomy of the equipment how it functions. But I showed you different geometries using which it can be like shear it can be in pure tension it can be like you know dual cantilever mode it can be bending it can be torsional I mean single cantilever or dual cantilever any of those again it depends on the type of sample you are handling with its relative stiffness its geometries. And then dynamic mechanical testing and extreme responses to extremities purely elastic delta is going to be 0 purely viscous delta is going to be 90 degree. So in between always your polymer however it is a polymer solution polymer meant higher molecular weight highest molecular weight rubber fiber intermediate molecular weight low molecular weight lower molecular plastic even lower molecular weight paints and adhesives it makes the same sense it will be somewhere between 0 to 90 degree again it depends I mean in which temperature and frequency you are trying to capture it with of course, Even if it is a low molecular weight at a very low temperature viscous component will be subdued by the elastic dominance there. So then different viscoelastic parameter DMA data and curve and what is important is what are the sweeps we can make it we can vary keeping one variable and rest of it constant namely frequency amplitude time and temperature.

When I talk about the amplitude closely I am referring to capture the structural changes and also to capture LVR linear viscoelastic regimes where my viscoelastic component I mean properties is not that complicated it is only a function of time. While if you cross that boundary you intrude into nonlinear viscoelastic regime where modulus is not only a function of time but also it is a function of deformation as well strain as well. So, frequency sweeps gives you a idea about several transitions sol to gel physical transitions cross linking non-cross linking which is a chemical cross linking also you will be able to capture gross master curve you can construct across the frequency. Once again extreme low frequency means longer time means higher temperature and that is what time temperature superposition principle says. Of course, you can vary time keeping rest of this constant you can probe into the gelation you probe into the cross linking you probe into the crystallization and what not using this either oscillatory rheology or even the DMA and temperature sweeps gives you a gross idea About across a you know bandwidth of temperature range of temperature how its dynamic properties is.

I mean where it stays. Tg can be measured some of the physical property Tg is very very important Tg is effects on cross linking although I did not elaborate that much effect of cross linking on modulus effect of temperature on viscoelasticity. So, so far so forth we try to give you gross idea about what oscillatory or periodic measurement means dynamic measurement means. so next lecture , we are trying to cover up master curve means like you try to generate using different different segments of analysis say parallel to geometry capillary is going to come up next capillary geometry that way cover the entire range of you know shear rate or frequency and try to see how you know shear stress varies or viscosity varies and that is what it is called you know master curve. Maybe it may be so possible there is one rheometer cover certain range another rheometer covers another range in between there is gray regions. So, you can always interpolate extrapolate using the time temperature superposition principle or principles like Cox-merz principle and you can overlay it and come up with a master curve and that gives you a gross idea about how your system is behaves in which neurological parametric model it fits in.

So, that you will be use of that model and try to design either your processing equipment or using that you try to predict once processed what is going to be the shape of the you know ultimate product you are going to get out of it. So, stay tuned most interestingly you try to understand the master curve in the next class and try to see its implication of it. Thank you very much.