Rheology and Processing of Paints, Plastic and Elastomer based Composites
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Lecture 10

ODR, MDR, RPA, PPR

Welcome to NPTEL online certification courses on rheology and Processing of Paints, Plastics and Elastomer-based Composites. Today we are in week 2, lecture number 2.4, where we will be covering ODR, oscillating disc rheometer, MDR, moving die rheometer, RPA, rubber process analyzer as well as PPR which is parallel plate rheology basically. So, once again grossly four major rheometers we shall be talking about. Once again about the keywords, it is all written here. I am not going to read it each and everything.

It is for your reference. While reading it and searching in the computer, you can always use those keywords to get some essence from the you know either from the book or journals or anything internet resources. So, so far so forth I talked about first generation and second generation particularly in the context of rubber high polymers. First generation if you recall was a plastometer just giving some you know force, load.

You try to see how much over a certain period of time what is at a temperature constant temperature what is going to the thickness size. It refers to plasticity always. The second generation was since it operates only at a lower shear rate regimes was mooney viscometer which actually embeds a rotor inside a rubber matrix and you give the temperature from outside and try to rotate it and see how much is the torque, how much is the resistance. So, that is refers to second generation rheometers. But point is that as I mentioned the limitation of mooney viscometer was post curing.

Once material gets cured, if you have a complete rotation, it will try to slip. So, after curing it is fine. You still can capture you know scorch time and cure time. So, for example, mooney value of 5 or 35 unit respectively. 5 refers to scorch, 35 refers to a curing.

So, next was how to get rid of the because many rubbers actually how it behaves after it gets cured, it will try to remain flat. If it remains flat fine, if you can capture the initial part you do not bother about the rest part of it. Some undergo marching because even if you cure it fully, it still undergoing increase of the torque. And some extreme cases it can revert back, it can undergo degradation or reversion. So, that characteristics if you do not capture in processing point of view, you would not be able to judge it how much time you should vulcanize it.

So, do I really really how much time my material will be withstanding excess of temperature conditioning say. So, in that essence ODR which is called oscillating disc rheometer was discovered which is called third generation rheometer. And here ODR you can always refer to a standard ISO 3417 where you get the details of the procedure, details of the machine etcetera. Once again in the cartoon you see operating principle, you have a chamber and that can be heated and here you can fit it with the rubber and that you embed the rotor and this rotor undergoes oscillation. Because if it oscillates even if it gets cured there is no question of slippage because this you know rotors are bit serrated also.

So then again same as mooney viscometer you try to monitor torque as a function of time. And that gives you clue about when it is curing. So, since it is a disc is used as a metallic biconical disk is used grouped serrated to get rid of any sort of a slippage whatsoever and you monitor torque as a function of time. And that is those this actually ODR is often referred to not a classical rheometer rather you can call it like a cure meter. It is all the way in rubber industries used to determine optimum cure time that means how much time it will be requiring for vulcanization to complete or curing to get complete.

So it actually gives you in addition to mooney after cure information that is the essence of ODR. So, once again I am not going into the details depending on type of rubber you are handling with, it can be small arc rotation oscillation and if the soft rubber you can still afford to go for higher say 5 degree. So it all depends what type of a system hard, soft, semi-hard or very soft accordingly you can select what is the angle of oscillation. And the forces used to oscillate if the disc is proportional to sample stiffness like I said here in this case the torque mooney viscometer as I mentioned it is a torque rather than the viscosity which was monitored. So it gives you idea about the curing characteristic like this.

So you try to see put the rubber from time 0 from 0 you monitor across the time. So once the rubber is inserted over a time you see it reaches a minimum torque we call it minimum viscosity in rubber language. And then the curing starts and all the way through it reaches the equilibrium time and there is a time which reflects up to that time with a given thickness this is the time necessary for curing your rubber or vulcanizing your rubber. Some of the essential part you get it from the curve is the minimum viscosity although it is not viscosity classically you call it minimum torque it is always deci newton meter maximum torque which is maximum here. And then T s 2 the 2 unit rise of the torque from the minimum viscosity or minimum torque and then T s 90 we often make our rubber convention 90 percent curing because before removing you end up spending some time particularly those rubbers which are vulnerable to you know reversion in that case T 90 is important.

$$\mathrm{CRI} = \frac{100}{(t_{90} - ts_2)}$$

But if it is a flat cure system does not really matter whether I cure 90 percent or I intentionally leave it like a little under cure or not ok. So that is the essence of it. So this is cure rate index that also you can that actually is a slope of this curve that rate cure rate basically this what is the slope of it that it refers to. So these are the some of the parameters which refers ideally what we need the torque versus time this is torque do not confuse with temperature I mean temperature. It should be like so you should have enough safety this refers to safety because you have to do some temperature treatment before finally shaping it after shaping you need vulcanization.

So flow is necessary that window of safety safety regime is we call it in our language cost type or safety time basically. Then the curing should be as fast as possible and then it should remain flat but it does not happen so. The real one is either like this this is called Plateau type of cure it can be revert it can be marching. So there are three different types of distinctly cure system depending on system you are handling with. Now point is that try to imagine the system you have you have both way rubber in between a rotor, metal is a good conductor of heat while rubber is not.

If it is filled with carbon black little bit good but if it is filled with silica it It is a bad conductor of heat and electricity everywhere. So that way there will be lag of temperature diffusion because provided you are providing heat from outside jacket. Not only that the removal the serrated rotor removal of it and then cleaning it after I mean one test to the other there will be there may be contamination. So these are the distinct limitation of it. The next generation of which was replacement of the rotor altogether rather than that you try to have a die and in that die in between rubber goes.

So you eliminate you know conductor to non-conductor to conductor that gradient basically. Once again you can afford to rotate the lower platen of it at certain degree arc the principle remains same and rest of the particle remains same and you call it MDR. But one important parameter you get it in MDR is you can resolve the torque in two components storage and loss. So in addition to the information about the cure you start getting another get another information the delta. Once again delta measures the viscous component of it.

So in addition to cure you get information about the viscoelastic properties of the rubber as such. Although all those rheometers starting from Mooney, Plastometer, Mooney, ODR, MDR all are dedicated rubber type of a rheometers and rather we will prefer MDR and ODR is more of a cure meter rather than you know rheometer. But still in rheometric sense you get some component like delta from MDR that is the point of. So you can see here if you look it at although it is well noted but you must be understanding two basic differences. One the heat lag you have sorted out, second removal of the sample you have sorted out and generally time required corresponding to MDR measurements is much shorter than ODR and that refers to the actual time.

So probing into the rest of the properties you get so one information tan delta and in additionally here also you can capture post curing information that also you can do it in ODR also that means marching, plateau and reversion type of a cure in sort. The next generation of it that means fourth generation of it was derived actually from MDR. In this case in addition to what you have done so far in you know MDR you can afford to there was limited to 3 degree arc you can afford to do more angular oscillation that means you can afford to do angular angle sweep also that means it is referred to amplitude. You can change the frequency of the test generally the test always for a mooney viscometer was 1 or 2 rpm 100 rpm for mooney viscometer 1 hz for say ODR. So here it is you can change the frequency.

Moreover you can change you know the temperature as well vary the temperature as well. Generally for ODR, MDR at a constant temperature you are doing the experiment torque as a function of time. So in a sense it becomes in a true sense rheometer where you can afford to do all these tests. These details of this test I will elaborate in the next class. What are the sweep you do normally for oscillatory rheometer and this is more of a oscillatory rheometer.

In addition to the determination of cure time, scorch time you can get more additional information of oscillatory rheology basically of the sample. So it gives you one hand information about the properties, cure properties in other hand it gives you information about the rheology and structural changes that it happens. Generally it always refers to rubber process analyzer which is RPA abbreviated there the alpha technologies they made it. But recently Montech is another company who made it similar to the machine but they named it because of the proprietary reason they call it DRPA. But machine in principle it works in the same similar basis basically and you can always refer to appended website here.

So RPA what I mentioned you just now you can probe into the processability, you can probe into the cure characteristics, you can also predict what is going to be the final properties. So that is the nowadays rubber process analyzer is very very must in most of the major manufacturing industries in rubber specifically. Once again I am not going into the details of it you always refer to alpha technology website you can always refer to Montech website, you can refer to standard books and bibliographic at your wish just type RPA, DRPA. So what you can do what is essential here in the anatomy of the machine sample mounting in the cavity temperature control system of it, it has a very precise temperature control plus minus 0.

3 degree. It has a servo motor that gives you the oscillation in terms of amplitude and frequency see it can always vary 0.05 to 90 degree arc. While in you know ODR and MDR it was limited to 3 to 5 degree arc maximum and it can operate 0.03 to 33 hertz always you can convert that hertz into the you know shear rate also. Then sample properties also so this is the servo motor that is making it different from that of the MDR basically.

So you can see if you compare MDR vice versa RPA because just previous generation was MDR it makes sense comparing it with that. In addition to cure information you got whole lots of those although it is a costlier more expensive as you can understand. But one most important thing you can do using RPA is non isothermal cure kinetics you can probe into the cure kinetics very easily how? You can make your program in such a way that you can gradually change the temperature while monitoring the torque as a function of time. So you get at different rates try to get it cured and use Ozoa or Finval Ozoa or other methodologies dynamic cure rate dependent from there you try to generate or estimate the activation energy. So suppose if in a company you are curing at 150 degree tomorrow it demands 160 degree centigrade what time you have to allow it for what should be the optimum cure one to the other, that interpolation extrapolation can be easily done once you probe into the non isothermal kinetics study specifically that you can pretty well do it with the RPA.

So in a sense temperature can be variable oscillation frequency can be variable strain angle can be a variable time either is a variable. So as it's mentioned variable temperature variable frequency variable strain and multiple program test also is variable and that always help you to probe into the viscoelastic properties of that polymer particularly rubber in general because it is as the name says it is RPA rubber process analyzer not only rubber but any amorphous materials you can deal it with high molecular weight amorphous materials I mean say for example if you ask me the question what is that material polystyrene is amorphous plastics. So you try to monitor the similar test at a higher temperature go pass the TGA and try to do that kind of a test. In addition as I mentioned you can do stress relaxation experiment you can give some delay in the program see how the structural changes structural recovery say filler is migrating from it is actually de-clustered and then clustering aggregating breaking of aggregates happening matrix properties structural breakdown combination of modulus torque viscosity actually next class I will elaborate what is the difference between viscosity and modulus. So that way not only you get a modulus information both storage and loss similar so you get information about the viscosity as well, Cure can be monitored pretty well under isothermal condition and that non isothermal condition as well.

So this is the typical you know non isothermal vulcanization behavior where you can probe into the kinetics of you know vulcanization and you can interpolate extrapolate the cure time and then you can do variable frequency analysis you can do variable strain analysis structural breakdown payne effect you can probe into that you can do many programmed analysis program is at your wish what type of a properties whether it is a rheological properties or dynamic mechanical properties that you would like to refer to. So now my last context is of today's lecture is parallel plate rheometer and so forth so forth up to RPA it was dedicated on rubbers but parallel plate rheometer you can do it for rubbers you can do it for plastics you can do it for fibers even you can do it for the low molecular weight polymeric material like suspensions their suspension paints adhesives and what not of course there is a window of frequency I mean different fixtures by which you can practice it that is what information you probe into. So let us try to understand what it is first a parallel plate rheometer is a type of rheometer uses to measure the flow properties of a fluid. So this is a classical rheometer not that cure meter so far I was talking about while dealing with you know ODR MDR or even RPA because RPA once again even if you get you know rheological information also that is very gross that is not that sensitive because it captures in one hand the dynamic properties in the solidus form as well it liquidus form so you can understand and there is a in a serration there is all sort of a precise determination of shear rate viscosity as a function of shear rate you may not get it from there so in that sense it is little truder in rheological sense. So to probe into the flow properties of a fluid parallel plate rheometer is one of the instrument along with the capillary rheometer to cover various regimes basically of shear rate not only that it gives you idea once you perform the oscillatory experiments you get into the viscoelastic you know behavior of it.

So two modes testing you can do it one is rotational mode and you can do is oscillatory mode also so oscillatory as I said already or as I am going to elaborate later it helps you to have the two components of viscosity one is storage another is loss. So it is easy to probe into the you know viscoelastic behavior of the material. So when a sample fluid is placed between the two plates the rheometer applies a shear stress either in oscillation or complete rotation. The resulting deformation or flow of the fluid is measured and analyzed to determine the rheological property that is what the basic principle is. So it is all written I already elaborated it.

So what is important here we have a very precise control of temperature, precise control over the stress and strain and the ability to perform the dynamic or oscillatory experiments that is the beauty of it. So how does it work in a rheological measurement stress strain and strain rate are all calculated signals basically. The raw signals behind the same is the torque. Torque is what is converted actually to either viscosity or modulus essentially.

I will show you with the example shortly. So angular displacement and velocity basically. From there its torque is derived and then fundamentally a rotational rheometer will apply to measure torque then angular displacement and angular velocity. Let us try to understand how we can do it. See the torque this is the rotation complete rotation r is the radius over which is rotating. So easily the torque you can measure if it is r f is the force applied here m equals to r dot f into sine theta which is the angle.

$$\mathbf{M = r \cdot F \cdot \sin\theta = r \cdot F}$$

So more of here in this picture it is 90-degree angle so r dot f. So you can easily derive the shear stress which can be calculated as m the torque I derived from here dot k sigma. What is k sigma? It is a geometrical stress factor stress constant basically. So you define here sigma m and k and you see m is actually derived m is nothing but the torque. Now the angular displacement theta if it is so in radian theta equals to s by r.

$$\sigma = M \cdot K_{\sigma}$$

$$\theta = s/r$$

s is the arc length and then r is the radius and you always radian to you know degree you can convert it 180 degrees pi radian always. And that way you can from the angle you can derive the strain which is theta that angle dot k y again k y is the strain constant. So that way you have captured sigma and gamma. And then how you get it the other parameters like shear rate say for example. So, you see if angular velocity is omega and theta is the angular displacement and then your omega is delta t by t delta t differential of it and from where you can very easily calculate gamma dot because when I refer to rheology gamma dot is the shear rate and which is omega dot k y and k y once again is a strain constant.

$$\gamma = \theta \cdot K_{y}$$

$$\Omega = \Delta\theta/\Delta t$$

So that way you can always refer to modulus or viscosity again in the next class I will just clarify you the thin line of boundary between modulus and viscosity. When I refer to solidus problem because remember polymer is viscoelastic whether to consider as elastic or whether to consider as a viscous. When I consider it more of like a solid I will always refer to modulus when I consider it still there is some viscosity I will always refer to like eta or viscosity term. Nonetheless you just refer to Hooke's law and simply refer to the Newton's law of viscosity. What it says modulus is stress upon strain from Hooke's law.

From Newton's law what you say the viscosity is again stress upon rate of shear. So that way from this relationship you can pretty well calculate both the modulus as well as viscosity. So if you do it again in a complete rotation manner you get absolute viscosity. But if I do oscillatory mode I get a two component of it storage as well as the loss component of it. And that I can probe into what is the delta factor again delta factor refers to the amount of liquidity or solidity it has.

So five important rheometer specification when you buy a rheometer you always look into the torque range. So that defines what type of a fluid I can handle with this rheometer. Obviously if you put it like in RPA the torque range was much higher because I was dealing with rubber which is a high molecule. It does not flow practical like a plastic it melts basically. Angular resolution see it giving you angular sweep but what is the resolution? Resolution means how precise it is.

And then angular velocity range that defines the shear rate you can accumulate there. And then frequency range and normal force. That is one another important thing you can get it directly from rheometer. See once a fluid is rotating I mean you have star r rotating on inside a fluid there is one phenomena called Weisenberg effect or lifting of effect because of the elastic component of it. See once you have a rheometer you have some pressurized things and you have bearing part.

From bearing you can directly measure the first normal force difference that is the beauty of parallel plate rheometer. So once again when use a parallel plate rheometer low, medium, high viscosity liquids you can probe into solid solid soft solids thermosetting materials sample with large particle suspension I talked about. And then temperature ramps you can do materials that may slip also here. And small sample volume you can do it very very small amount. Again parallel plate rheometer you can calculate r by h r is the radius of that you know plates and h is the gap and stress constant also as I mentioned.

Strain Constant: $K_\gamma = \frac{r}{h}$

But bottom line is that as diameter decreases the shear rate increases and this is the formula you can always refer to. For gap decreases again shear rate increases again it all depends you have to do little bit of optimization what type of a gap and plate size you have to choose for. And most strictly of it relies on the viscosity or rheological properties of the fluid you are going to handle with. So as you can see from the certain as you know rotate it the fluid between the two plates you can measure its rheological properties but there is a limit. If you rotate it way too high angular velocity this fluid front is going to split from here because of the centrifugal force.

So that is the limitation in terms of you know and then accordingly you have to adjust the gap because it is a capillary effect that tries to hold the fluid together and on the contrary centrifugal force it will try to detach it. So one of the limitation of course of parallel plate rheometry is it depending on from the center position of the rod I mean where it is rotating it is rotating here from one point to the other there will be change of the shear rate of it. So it is exactly not I mean it is so shear rate dx is the you know increases further from the center and it stays constant. So this is one of the way you can look it at. So that is what actually gives you the genesis of cone and plate rather than parallel plate where you have a conical shape of the one of the part of the plate.

So that actually pretty much takes care of this geometry the gradient of variation of shear rate from the central position to the other. So that is one of the beauty of it. So once again the parallel plate viscosity can be corrected through the Weisenberg you know Rabinowitsch equations basically. So if you actually take it into consideration depending on the exactly which point you are considering if you apply Rabinowitsch correction which takes the form I am not going into the details of it but of course what you get a output from a cone and plate and a parallel plate then you can superimpose it provided you do the Rabinowitsch correction Weisenberg Rabinowitsch correction that is what it is. So again cone and plates you can calculate the strain constant, stress constant those I showed you already and then accordingly you can calculate out the shear rate, shear stress so on and so forth.

And also this is truncated gap this is also this plays significant role in parallel plate rheometer as I mentioned the height you can afford to change it but here you really cannot you have that that is already pre decided here depending on of course so depending on suspension type this cone angle actually will vary. So that is also another part of it. So when to use cone and plate over parallel plate very low to high viscosity liquids high shear rate measurements higher than parallel plate measurements I showed you the limitation that width part can split actually at a higher angular velocity. And then the normal stress growth unfilled sample isothermal test small sample volumes. So this also I was talking about with the you know as diameter decreases shear stress increases and cone angle decreases shear rate increases again I mean that you can see it from the at 2 degree to 0.

5 degree of the cone. And this is a very very small angle actually although it is a cone but it is a very shallow angle just to take care of the gradient of shear rate. So accordingly you can calculate again in terms of suspension depending on the suspension type you are handling with you have to choose this angle. With the larger particle suspension small particle suspension your choice will be different because you have to make it sure that particular particle large particle should not get compressed so that effect will come into prominence at this curtain source. So this is also very important particularly dealing with the rheology of suspension. So again you have to pick choose exactly which is the correct filling liquid filled samples over filled system so there will be additional contribution will come.

So there are certain things which you can see when you compress a fluid then some fluid will be non-load bearing type. So that drag will try to come as an error to your absolute determination of shear stress as a function of shear rate. So in that case there is also a solution. Solution is a concentric cylinder what it is exactly this one cone and bob type bob and you know this type cylinder type cup. So in that essence this brown one is showing is a fluid and you have a rotor here and it is rotating and there is no question of you know splitting of the fluids neither the evaporation that may be a problem for if you say try to analyze the solution there will be evaporation of solute may possible.

So in order to further correct the wall slippage or drags you have rather than this geometry this geometry is there but what is the difference between that you see the in between the fluid it is there. So in this case that heat transfer also is going to be a problem a drag is also going to be a continous slip will be more rather higher you know contributed there. So that can be the next generation this if it is one initial geometry that this geometries number two is much preferred one in that essence that is called double wall concentric cylinder geometry. So these are the strain constant stress constant as I already elaborated you and accordingly you can see it for double wall it changes all it depends on this if I see precisely r 1, r 2, r 3 and this height that these are the geometric constant for single wall and of course the double wall ones those configurations. So when you use a concentric cylinder low to medium viscosity liquids you can probe into unstable dispersion and slurries also which you apparently cannot do with a parallel plate or a cone and plate.

You can minimize the effect of evaporation if your solvent is evaporating type, weakly structured sample and high shear rates. So much larger shear rate you can afford to have it compared to that of parallel plate and cone and plate here over here. So if you just have a gross comparison between different types I elaborated so first starting from parallel plate, cone and plate, Couette which is actually a concentric cylinder that is elaborated whether it is a double or single, torsional rectangular type and DMA Which I am going to cover first. From the application point of view what you should choose for cone and plate viscosity should be greater than 10 millipascal second, parallel plate greater than 10 millipascal per second whereas in this thing even less than that low viscosity less than 10 millipascal second you can handle with even with a double wall because of you have a less contribution of wall slippage and you can go to the less than 1 millipascal second type of a fluid. Torsional one for the solid polymer DMA generally grossly meant for high molecular weight polymers basically high viscosity of course.

So you can see the advantages and respective disadvantages and accordingly as per your wish you try to pick choose it here you can refer to that you know the website where from you get some additional resources. Once again my bibliography remains same that I had talked about earlier no change from there grossly what I covered up ODR, MDR, RPA and then a classical rheometer which we grossly call it like a cure meter. Of course RPA is more like a rheometer as well but although its values are not that precise remember. Parallel plate rheometer is one of the rheometer of course up to a lower shear rate regime lower means compared to capillary that I am going to cover up in my third week of the lectures. But essentially what I touched upon how does the rheometer works when the parallel plate rheometer is used what is the correction factor that you have to do it cone and plate.

When to use cone and plate over parallel plate limitations then when I have to really go to the concentric cylinders geometry and of course the double wall is better than the single wall in that essence. So then the geometric review. In the next classes I am going to talk about DMA in light of rheology. So I have always referring to DMA dynamic rheological properties oscillatory rheological properties like say parallel plate can work in both full rotation or oscillation. So what is the difference between DMA classical DMA and oscillatory rheology in general we are going to touch upon in the next lecture till then thank you very much.