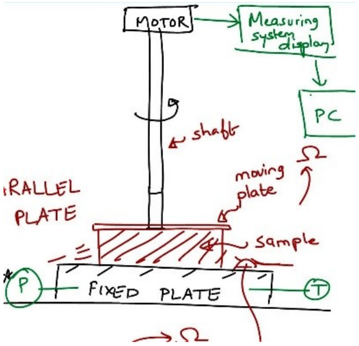
Introduction to Polymer Physics

Dr. Prateek Kumar Jha
Department of Chemical Engineering
Indian Institute of Technology-Roorkee

Lecture-57
Rheometers and Rheological Tests- I

Welcome all of you so in the last lecture we have been discussing about the idea of Rheology and what exactly we require in a Rheological experiment that is what we said that we either apply stress and measure the shear or shear rate or we want to get to a certain shear or shear rate we maintain that and then measure the amount of stress that is required for achieving that. So, today I will talk about the instrument that does these things for us. We already have discussed a table tab table top setup that is not quite practical. So, we will talk about a more practical or commercial instrument that is used to measure Rheology that is the Rheometer.

So, there are varieties of Rheometers in market now but all of them share few common features that is what we will discuss today. One is that we have some sort of a fixed plate there are some dual drive instruments now that does not have a fixed plate but this is the most common instrument and then we have a rotating shaft that is connected to a motor and this shaft is attached to some sort of measuring geometry and that geometry basically either confines the sample or it is like sitting over the sample depending on what the geometry is like. So, one of the most common geometries look something like this you have a plate here and then the sample is placed between the plate and the fixed plate is the moving plate so of course the plate is also rotating as the shaft is rotating, the plate also is rotating with certain angular velocity called Ω.



This will be the side view if I do the top view from the shaft side what you will see is essentially only the moving plate that is rotating with some angular velocity Ω and that is of course over the sample just like a disc that is moving like this and the sample is placed this is my fixed plate here is my shaft and then a disk is connected to a disc like thing and the disc is rotating now whatever sample is confined undergoes a shear because the top plate is moving relative to the fixed plate.

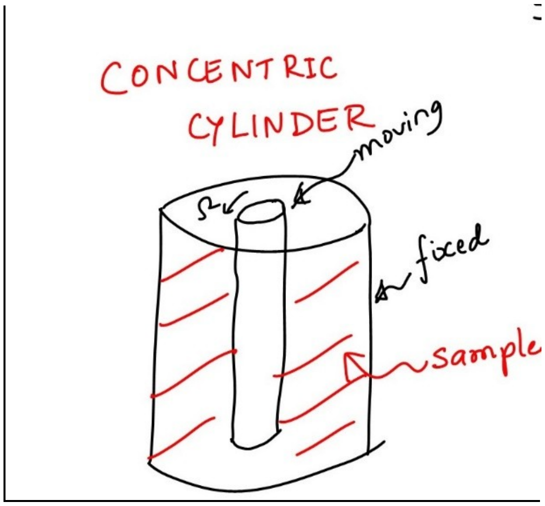
So, the advantage of this kind of a thing as opposed to say applying shear by this means now we are applying shear by rotation so now the advantage is like no matter how high the angular velocity is the thickness of the sample can still be the same we do not need a very large setup as in the case of applying shear like this as I was telling in the last class applying shear in this way this way if I go to a high shear rates we need a very large workspace. In this case since the sear is applied by rotation I can apply a very large rotation but still the amount of confined sample will remain the same. This is like one of the setups, this is the parallel plate geometry and then typically there are other controls that you can do if you want to do experiments at various temperatures you will have some temperature controllers attached to it you may also have a pressure controller and of course you will have some measuring system display nowadays most of it goes to a PC where the software can do all sorts of stuff apart from simply measuring the force applied.

So, actually the force applied for the rotation if I divide by the area of the plate it gives me the stress. The software has the proper calibrations and formulas built into it they will provide you the stress versus the amount of shear or shear rate that you have in the material. So, it is like nowadays fully automated setups that can give you these things and then you can also fit various types of models that all software's can do it for you and you can also design several types of test protocols depending on the type of material. So, if you want to say apply a constant stress you can do that if you want to apply a constant shear rate that is also possible. So, you can program using the PC typically how you want to conduct the experiment but the basic output remains the same that is –

$$\sigma = f(\gamma, \dot{\gamma})$$

Where this can be Or/AND depending on the type of material or the type of test that is being conducted on the sample.

So, there are others geometries- One of the geometries is called a concentric cylinders geometry that is very common for the case of liquids especially liquids that are viscous in nature. So in that the idea is that there is there are two cylinders again it is connected to the same arrangement. So, you can detach one of the attachment and attach another, so same setup can do both parallel plate and concentric cylinders depending on the number of geometries that you have. So, in this case you have a cylinder that is typically fixed and then you have a cylinder concentric to it which is moving and then your sample is constrained between the two, just mean because two cylinders. So, if I look at the top view this will be my outside cylinder this will be my inside cylinder which is moving with Ω and then my sample is right here.



So, now as opposed to a parallel plate set up where you can imagine that the sample can overflow from here. So, you have to find a way to trim those ends and be careful that the plates maintain a contact with the sample at all the time. In this kind of a thing of a concentric cylinder that is not a problem because it is always confined between the two cylinders which are concentric to each other depending on the requirement there are other geometries that also work such as the cone and plate. So, now you have a plate that is rotating and it is connected to the shaft and then you have the fixed plate and the sample is confined in between the two.

So, these are the kind of tests we can do and for all these different geometries the slightly different formulas will apply and the software's will typically take care of it but if you want to interested you can read books on Rheology they will have detailed derivations I am not really going into all the details here we want to just talk about the practical aspects that are important in the Rheology.

So, now and as I have already said the basic theme is we apply some stress that can be time dependent and we measure the response in γ_p AND/ OR $\acute{\gamma}_t$ or we can do a opposite of this, we can apply the γ_t or $\acute{\gamma}_t$ and measure the stress that that you have there.

So, one of the experiment that can we can do is for example the Step strain in here what we do is with time I will apply shear γ that is the function of time that is essentially a step function that essentially goes like something like this. So, you have γ_0 beyond t = 0, so we can say –

$$\gamma(t)=\gamma_0\theta(t)$$

$$\sigma(t,\gamma_0)=G\gamma(t)$$

so we can say γ_t is $\acute{\gamma}$ step function θ of t. So, in this particular case if I measure the stress, stress will be a function of time and the stress will be a function of the $\acute{\gamma}$ that is the maximum shear that is being applied and then this can be written as something like a G multiplied by γ of t and then this G is what is known as the elastic modulus or so as not to confuse with the Young's modulus and all that it is preferable that we use the word relaxation modulus.

So, now the things become easy if there are and there is a certain approximation that works and that is the material is linear viscoelastic that basically captures even the materials which are Newtonian and so on. For nonlinear viscoelasticity we will have a different class of equations but for linear one that is a wide class things are relatively easier. So, we have linear viscoelastic material when it follows what is known as superposition principle, just true for linear viscoelastic material and what the superposition principle demands is if for example I do two different experiments in one of them I measure the stress for applied shear γ_1 and I get the stress has σ_1 as a function of time similarly if I do another experiment with shear γ_2 and if I get the stress σ_2 (t) what it means is-

$$\gamma_1(t) \rightarrow \sigma_1(t) \wedge \gamma_2 \rightarrow \sigma_2(t)$$

It means is this 2 will imply that if I conduct a new experiment where I apply the sum of these 2 shears I should get the sum of those 2 stresses.

$$\gamma_1(t)+\gamma_2(t) \rightarrow \sigma_1(t)+\sigma_2(t)$$

So, this is like the requirement that the linear viscoelastic materials must satisfy in order to apply the equations that I will discuss next.

So, if this is true then what we can say is we can talk about any general type of deformation, let us say we are looking at some profile of γ_t versus t, I can divide this entire time domain into small intervals. Let us say this is my Δ_t and the meaning of these intervals. So, let us say called Δ_{ti} for the i^th^ interval and within that interval. If the change in the shear is $\Delta \gamma_i(t)$ then this would give rise to some stress σ_i (t). So, just like I can sum the small shear amounts for the different Δ_{ti} to get the totals here at any point we can also simply sum the small stresses that are coming as a result of these small changes and then I can get the final stress acting at a given time.

So, the first part of it does not really require the superposition principle. All we are saying is the change in the shear that we are looking at the change in this here –

$$\Delta \gamma_i = \acute{\gamma}(t_i) \Delta t_i$$

$$\Delta t_i = \Delta t \wedge \Delta \gamma_i = \acute{\gamma}(t_i) \Delta t$$

if I want to keep the Δ_t constant so Δ_{ti} is held constant then $\Delta\gamma_i$ is $\acute{\gamma}$ (t_i) Δ_t and if I am representing this time point as say t_i then the effect of that $\Delta\gamma_i$ would appear at all times past this t_i and the effect of that will of course do not will of course not come in the times before this particular t_i. So, what I can then write is –

$$\sigma_t = \sum_i G(t-t_i)\Delta\gamma_i$$

Of course before that time there was no $\Delta\gamma_i$ applied the effect of shear applied at time t_i will come into picture only for time after that. So, if I simply keep on adding all the $\Delta, \Delta\gamma_i$'s before a particular time I can get the total stress at that time by the superposition principle. So, this I can approximate as-

$$\sigma(t) = \sum_i G(t-t')\acute{\gamma}\,\Delta t_i$$

And then in the limit Δt_i that is assumed to be Δt is going to 0, I can write-

$$\sigma(t) = \int_{\infty}^{t} dt' G(t-t')\acute{\gamma}(t')$$

This is the equation that is valid for a linear viscoelastic material where since we have defined my stress as G multiplied by γ where G is the relaxation modulus so this entire function becomes my relaxation modulus and what is key here is that if the material is linear viscoelastic then it is completely characterized by the single function G of (t).

Now let us see this relation in some detail, so I started with minus infinity just to account for all the history before this time because we all know we do not want to define an origin of time we go to the back in time because in any case the memory will only be affecting the system at least for liquids only for certain amount of time but the shear history we have to see from the beginning of time or when the experiment was started. So, this will be something like that –

$$\sigma(t)=\int_{-\infty}^{t} dt'G(t-t')\acute{\gamma}(t')$$

if now for example we think of any other experiment let us say if I am doing an experiment like this where the $\acute{\gamma}$ instead of γ earlier is changing like a step function like $\acute{\gamma}=\acute{\gamma}_0\theta(t)$. If I plug in there in that function what I will have is –

$$\sigma(t)=\acute{\gamma}_0\int_{0}^{t} dt' G(t-t')$$

Now we can define $(t-t')$ as t'' this would give me - t'' as dt'' and this σ_t then would be the limits are changed. Now so-

$$\sigma(t)=\acute{\gamma}_0\int_{t}^{0} -dt''G(t'')=\acute{\gamma}_0\int_{0}^{t} dt' G(t')$$

So, I can use the minus sign to switch the limits and then I have so t'' was dummy variable anyway. So, I just changed to some t' , so in this case what do we see we see that the σ_t will keep on increasing but it cannot really increase to infinity. So, what does that mean that we have an infinite stress in the system at least in the case of liquids, for the case of solids probably if I apply a very large stress then the material should pretty much break. In the case of a liquid however there is no counterpart force a very high stress very high stress so ultimately give rise to some kind of viscosity that should eventually become constant. So, it cannot be that if I keep on increasing the stress the viscosity should keep on increasing or decreasing whatever ultimately it has to reach any steady state value and this is what we refer to as the steady state viscosity so in the very beginning for any material you might see that on the application of this $\acute{\gamma}$ in the very beginning the viscosity may come out being different but eventually the viscosity must settle to a certain value that would be the steady state viscosity value depending on the material the amount of time it will take to reach steady state can be different. So, this viscosity can be defined as –

$$\eta_0=\int_{0}^{\infty} dtG(t)$$

But that is only true for the case of a liquid for the case of a perfect solid of course the steady-state viscosity has no particular meaning. So, now it if I look at the last two tests that I have discussed the first test I discussed was a step strain where I at time t =0, I started applying a certain strain or shear and the next text test that we have discussed is a step shear rate but essentially at time t = 0 we start applying some shear rate both these tests will work for different class of materials. The first tests were work for class of for solids and the second test will work for liquids if I want to say look at a viscoelastic material then what these tests are not quite enough. We need to find a mechanism where I can vary both γ and gamma dot because then only we can get σ as a function of both γ and $\dot{\gamma}$ in a given experiment. So, in both these cases we are not really changing both γ and $\dot{\gamma}$ simultaneously. So, we cannot get σ as a function of γ and $\dot{\gamma}$. So both these tests will only work for the case of a perfect liquid or a perfect solid the first one for solid the second one for liquids.

But there is a mechanism where I can achieve both in a single experiment and that is when instead of applying a step shear or for a step strain what I do apply is sort of an oscillatory shear or an oscillatory shear rate and this is what is most used to characterize the polymeric materials with viscoelastic behavior. So, in oscillatory shear what we do use is I will apply the shear using this particular function and we get –

$$\gamma(t)=\gamma_0 \cos \omega t$$

$$\dot{\gamma}(t)=-\gamma_0 \omega \sin \omega t$$

So, we will have both γt and $\dot{\gamma} t$ that is a function of time and the difference here is both are like out of phase with each other. The second one is like a 90 degree out of phase with the first one and therefore we will see both these kind of responses in the experiment. We can look at the σ (t) that would now be a function of both γ and $\dot{\gamma} t$ because both of them are now varying within the experiment as opposed to the previous case.

The only thing that we have to be careful is we typically use what is known as a small angle oscillator shear because sometimes the further approximations that we make will not be valid if I apply a large angles shear. If I apply more shear when given point it has also to do with the fact that the linear viscoelasticity itself is an approximation that would only work for small shears as opposed to large shear's.

So, in the next class I will do the example of the oscillator shear and then we derive the expression for what is known as the complex modulus which contains both the liquid contribution and the solid contribution and essentially characterizes the amount of viscoelasticity a material poses.

So, with that I conclude here, thank you.