Introduction to Polymer Physics
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Lecture-58
Rheometers and Rheological Tests- II

Hello everyone in the last lecture we have been discussing about different Rheological tests. We looked at the constant shear test, the constant shear rate test and while the first one was for solid samples, the second one was for liquid samples and then finally we talked briefly about oscillatory tests that can give you a viscoelastic behavior by looking into both liquid and solid like behavior in one go because in that test both the shear and the shear rate varies with time. So today I will take it further and then try to elaborate on how can we separate the liquid and solid contributions in a Rheological tests.

So, basically what we have discussed in the small-angle oscillatory shear or the small amplitude oscillatory shear is that we will have the shear varying with time by an oscillatory function in fact that is a general oscillator shear if it is like a smaller magnitude then actually the linear viscoelasticity holds that is why I add the word small amplitude then in that case we will have –

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

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

And both of them are out of phase by 90 degrees. So, therefore we can look at both the change with γ and $\acute{\gamma}$ as two phases of the wave.

So, in this case if I use the formula that we have got from the superposition principle that is for the case of a linear viscoelastic material what we do get is the following. So, this was the formula that we have derived in the last lectures and this is going to be in the case of oscillatory shear-

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

$$\text{¿}-\gamma_0\omega\int_{-\infty}^{t} dt' G(t-t')\sin\omega t$$

So, now I will do a change in variables, so I will define $t-t'$ as my t'' that would give me - dt' as dt'' and what I will get is –

$$\sigma(t)=-\gamma_0\omega\int_{\infty}^{0}(-dt'')G(t'')\sin\left[\omega\left(t-t''\right)\right]=\gamma_0\omega\int_{0}^{\infty} dt'' G(t'')\sin\omega(t-t'')$$

And if I do the math what I have is right now we get is –

$$\sigma(t)=-\gamma_0\omega\int_{0}^{\infty} dt'' G(t'')\sin\left[\omega\left(t-t''\right)\right]$$

$$\sin\left[\omega\left(t-t''\right)\right]=\sin\omega t\cos\omega t''-\sin\omega t''\cos\omega t$$

Therefore we get-

$$\sigma(t)=\gamma_0\omega\int_{0}^{\infty} dt'' G(t'')\sin\omega t''\cos\omega t-\gamma_0\omega\int_{0}^{\infty} dt'' G(t'')\cos\omega t''\sin\omega t$$

So, now what you can notice is this integrands this entire thing here is a constant because we are integrating for t'' going from 0 to infinity. Similarly this is also independent of time because we also integrate from 0 to infinity both of them actually are a function of ω. So, essentially I can write this thing as some G' ω and this entire thing I can write as some G'' ω where G' and G'' are new functions of ω they are not the derivatives of G. So, with this idea I can write this as-

$$\sigma(t)=(\gamma_0\cos\omega t)G'^{(\omega)}-(\gamma_0\sin\omega t)G''(\omega)$$

Now since cos ωt is in phase with the applied shear that is γ_0 cos ωt and the sin ωt is in phase with the applied shear rate because that is – ω times γ_0 sin ωt what we can think of is this would be something that is of the sort G γ and this is something of the sort η $\acute{\gamma}$. We have –

$$\sigma(t)=G\gamma-\eta\acute{\gamma}$$

So, the first one is Gγ and the second one is $\eta\acute{\gamma}$ and therefore I can think of G' (ω) to be a measure of the elastic behavior and therefore I will call it storage modulus it characterized the elastic behavior. And the second term G'' (ω) refer to some sort of a liquid behavior because it is in phase with $\acute{\gamma}$ this I will call as a loss modulus and it characterized the viscous behavior.

So, the first one characterized the solid nature or a solid like nature and the second one characterized a liquid like nature. So, by doing a single test I can get both G' (ω) and $G^{''}(\omega)$ and of course the test can be conducted at different frequencies so essentially we get a function of frequencies for both storage and loss modulus and they would then characterize the liquid and solid nature of the sample.

So, now we can go a step further and define what is known as a complex modulus using the rules that we use in complex mathematics and what we do is we recall that-

$$e^{i\omega t}=\gamma_0\left[G^{'}(\omega)\cos\omega t-G^{''}(\omega)\sin\omega t\right]$$

$$¿\gamma_0 R_e\left[G^{¿}(\omega)e^{i\omega t}\right]$$

Where $G^{¿}\omega$ is defined as G' ω+ i G'' ω and we can say why this should be the case because if I do $G^{¿}\omega$ $e^{i\omega t}$ that is going to be equal to

$$G^{¿}(\omega)e^{i\omega t}=\left[G^{'(\omega)}+iG''(\omega)\right]\left[\cos\omega t+i\sin(\omega t)\right]$$

If I look at the real part of this the first term will come from the multiplication of this and this and the second term will come' multiplication of this with that because i multiplied by i is - 1 and what we do get-

$$\omega t - \text{¿} G''(\omega) \sin \omega t$$
$$R_e\left[G^{\text{¿}}(\omega) e^{i\omega t}\right] = G'(\omega) \cos \text{¿}$$

So, instead of working with two functions I can work with one function that is complex in nature and in that complex function the real part is my storage modulus that characterizes the solid nature of it and the imaginary part is my loss modulus that characterizes the liquid nature of it and as I vary the frequency essentially what I am doing is I am looking at the response to different amounts of shear or shear rate because γ is γ_0 cos ωt that will change as I change γ and also the $\acute{\gamma}$ is - ω multiplied by γ_0 sin ωt that is also changing with ω. So, essentially we are looking at the behavior for different applied shear or shear rate by simply changing the γ value.

So, simply the functions G' and G'' characterize the behavior of the system that is viscoelastic in nature of course if it is Newtonian liquid, and in fact any other liquid that does not have with no solid nature what we do get is that the G' ω will be 0 for all Omega values. Similarly if I have a perfect or Hookean solid and in fact any solid with no liquid nature what I will get is G'' (ω) = 0 for all gamma both of them are indeed the extremes for the polymer systems. We always get some finite values for G' (ω) and G'' (ω) that characterized the fact that polymers are both a liquid light material and a solid light material depending on the relative magnitudes of that we can comment on how liquid like or solid like that is so let us say if I look at something of this sort –

$$\left|\frac{G'}{G''}\right| = \frac{solid-like}{liquid-like}$$

If this term is high it means if it is much higher than 1 we say that the material is mostly a solid if it is much smaller than 1 then we can say the material is mostly a liquid. If it is comparable to 1 we can say it is viscoelastic and in there it can be a viscoelastic liquid or a solid depending on the magnitude of this quantity and this essentially is some sort of the phase of the complex modulus that characterize the relative contributions of these two things.

Now we can look at an example function where we have relaxation modulus that is given like some sort of an empirical function and now I want to find the complex modulus for this case. So-

$$G(t)=G_e+G_e^{\frac{-t}{\tau}}$$

$$G^{\text{¿}}(\omega)=G^{'}(\omega)+iG^{''}(\omega)$$

$$\text{¿}\omega\int_0^{\infty} dt^{'}G(t')\sin\omega t^{'}+i\omega\int_0^{\infty} dt^{'}G(t^{'})\cos\omega t^{'}$$

$$\text{¿}\omega\int_0^{\infty} dt^{'}G(t^{'})\left[\sin\omega t^{'}+i\omega cos\omega t^{'}\right]$$

$$\left[\sin\omega t^{'}+i\omega cos\omega t^{'}\right]=i\omega e^{-i\omega t^{'}}$$

$$i\omega e^{-i\omega t^{'}}=i\omega\left[\cos\omega t^{'}-i\sin\omega t^{'}\right]$$

$$\text{¿}i\omega\cos\omega t^{'}+\omega\sin\omega t^{'}$$

$$\text{¿}\omega\left[\sin\omega t^{'}+\left(\cos\omega t^{'}\right)i\omega\right]$$

So, we can then write this as-

$$\omega\int_0^{\infty} dt^{'}G(t')\sin\omega t^{'}+i\omega\int_0^{\infty} dt^{'}G(t^{'})\cos\omega t^{'}=i\omega\int_0^{\infty} dt^{'}G(t')e^{-i\omega t}$$

So, now we can use the function that we have defined G (t) is Ge + G multiplied with the exponential of $\frac{-t}{\tau}$ in this particular function and what we do get is-

$$G^{\text{¿}}(\omega)=i\omega\int_0^{\infty} dt^{'}G(t')e^{-i\omega t}$$

$$\text{¿} i\omega \int_0^\infty dt' \left[G_e + G_e^{\frac{-t}{\tau}}\right] e^{-i\omega t}$$

$$\text{¿} i\omega \int_0^\infty dt' G_e e^{-i\omega t'} + i\omega \int_0^\infty dt' G_e^{-t\left(\frac{1}{\tau}+i\omega\right)}$$

So, I can use if I integrate this what you will get is something like $\frac{G_e e^{-i\omega t}}{-i\omega}$ and then if you look at it, this will become a complex number. So, applications of limits become difficult here, so we use a trick here that will be clear once we do it. Instead of doing that what we do, so will not do this, what we do is we write the function that we have there as something like this –

$$\text{¿} i\omega \lim_{s\to 0} \int_0^\infty dt' G_e e^{-i\omega t' - st'}$$

$$\text{¿} i\omega \lim_{s\to 0}\left[\frac{G_e}{-i\omega - s} e^{-(i\omega+s)t'}\right]_0^\infty$$

Now you can see that since I have added a small s here the upper limit now goes to 0 and the lower limit of course goes to 1. So, adding the real number essentially makes our job easier. So, this then gives me –

$$i\omega \lim_{s\to 0}\frac{G_e}{s+i\omega} = G_e$$

We can look at the second term in second term we already have a real number. So, there we do not have any problem. So, that will be-

$$\frac{G}{i\omega+\frac{1}{\tau}}$$

So, now if I further simplify it what I will get is –

$$G^{\text{¿}}(\omega) = i\omega\left[\frac{G_e}{i\omega} + \frac{G_e(i\omega)}{-\omega^2-\frac{1}{\tau}} + \frac{\frac{G}{\tau}}{\omega^2+\frac{1}{\tau^2}}\right]$$

$$¿\left(G_e+\frac{G\omega^2}{\omega^2+\frac{1}{\tau^2}}\right)+\left(\frac{\frac{i\omega G}{\tau}}{\omega^2+\frac{1}{\tau^2}}\right)$$

So finally

$$G^{¿}(\omega)=G^{'}(\omega)+iG^{''}(\omega)$$

This is how we can really go this is how we can really go in any kind of an example if we have the relaxation modulus given or if it is like an empirical function that we can even try to fit using the experimental results. We can get the forms of $G'(\omega)$ and $G''(\omega)$ for that relaxation modulus and then if I try to fit using the experimental data we can see whether the empirical model that we started with is correct or not. So, in this particular case you can note that in the relaxation modulus the first term is a constant and the second term decays with time. So, the first term has to be a 0 for a liquid and even for a viscoelastic liquid that eventually at very high times will go to a liquid like a state because then it should not have an elastic modulus the second term in any case characterize the liquid nature of it and the first term characterize the more or less the solid nature of it more or less speaking in the end it is ultimately what fits the experimental data best than what should be an appropriate function because you have a whole diversity of rheological behavior that you can possibly have.

So, before we go any further let me just tell you that the in the polymer systems you do not always have a linear elasticity you also can have a nonlinear elasticity that is also very common. So, if for example my η that is the viscosity that we often also call the apparent viscosity in the language of Rheology if this happens to be a complicated function for example containing terms like something like these-

$$\eta(r)=\frac{f}{1+\left(\frac{\acute{\gamma}}{\acute{\gamma}_c}\right)}$$

Then these systems will not show behavior that is linear in nature and in that case we can still talk about linear viscoelasticity in certain limits of maybe a small shear rates but the system's overall will not follow the linear viscoelasticity. So, all the kind of maths that we did and actually the starting assumption of superposition that we have used to write the expression for the stress tensor this is not going to hold for nonlinear viscoelastic models.

So, the key messages we have to apply some caution it is not that the storage and loss modulus cannot be found for the case of polymeric systems, the experimental protocols have this machinery built into it but the expression for the shear stress that is obtained using the superposition principle is not going to be valid. We will have more detailed models to find the stress in terms of the modulus and that is what I am not discussing in this course.

So, with that I want to conclude this lecture in the next lecture I will talk about a simple viscoelastic model that is called a Maxwell model that is used by people working in Rheology in analyzing the viscoelastic behavior of systems what we will notice is that that particular model is not really coming from the molecular principles that we have been doing in this course. This model is rather phenomological in nature knowing that the system shows a viscous behavior and an elastic behavior we can try to build and another class of toy model that is completely phenomological in nature not starting from the molecular models.

So, before we really conclude here what I also want to mention is that ultimately going from the equilibrium properties and thermodynamics to Rheology we have come really a very long way and what we have not really explicitly mentioned is the scales of applicability of those theories when we are doing a Rheology we of course are not looking at a molecular level. At the molecular level the whole idea of the flow and deformation the way we have been talking about does not really make as much sense as at the level of larger macroscopic samples of course when we are doing Rheological tests we are doing on samples of sizes of millimeters or centimeters at least and therefore we have been, over the passage of time in the course we have been developing more and more larger scale theories that are relatively less accurate but they cover different kinds of phenomena.

So, this is the whole approach I would say is sort of a multiscale modeling approach we started with molecular models when we were interested in behaviors such as Brownian motion diffusion the size of a polymer chain and so on. We start talking about continuum mechanics when we look at the overall flow and deformation of the system. The reason why these two models look very different is not really that there is any new physics that is happening there and is not happening here but what is more important is that we have no direct way to link the molecular models to say rheological or flow and deformation models.

So, there are efforts in that direction. So, now we can do for example molecular dynamics and try to get viscosities and so on. But those efforts still are limited to very small systems and not yet came in the field of polymers a whole lot you can do molecular dynamics and get the viscosity of a sample but those samples will be much smaller than what you can put into a Rheometer and that is the reason why we have been doing rather approximate or phenomological models which are relatively less accurate but explain physics at larger length scales then compared to the molecular models and in this course you have seen a very nice bridge between all these class of models because we started from a Rouse model using that we obtain the expression for viscosity even if we knew that it did not capture the effect of entanglement and so on and we discussed detailed models in that direction but at least is what it was some effort in that direction so the polymer physics essentially is multi scale to that extent because we try to use molecular models in various contexts as much we can and then finally when we give up we go to the phenomological models.

So, with that I want to conclude here and in the next lecture we discuss the phenomological Maxwell model that explains the viscoelasticity of polymer systems, thank you.