Introduction to Polymer Physics

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Lecture-56
Rheology of Complex Fluids

Welcome all of you in the last week of lectures we discussed about the flow and deformation in polymeric systems more from a theoretical point of view. We looked at how we can write the governing equations first beginning from the principles of continuum mechanics that is what is called a macroscopic definition of a stress tensor then we look at the same thing from a microscopic viewpoint using what is known as the microscopic definition of a stress tensor where we had the actual particles of solute present in the solvent and then we applied that model to look at the stress tensor for a polymer chain and then towards the end we discussed the effects of entanglement and so on.

It turns out that ultimately the key problem in studying the polymeric system is not that the equations of motion are not laid out but the problem is that the constitutive equations are difficult to derive and even if we derive the constitutive equations they will have certain material parameters that are very difficult to get without doing experiments. So, now I will talk about the subject of Rheology that tries to achieve this objective first we can get the constitutive laws for systems we do not know about and second we can get the material property that goes into constitutive relations that we have discussed.

So, this is not really a subject that is unique to polymer science people who have done fluid mechanics course must have read this in the context of complex fluids. The wave materials deform differ from material to material, a toothpaste behaves differently from a shampoo, a shampoo behaves differently from a solution of a cornstarch. And in fact if you want to look at the whole diversity or of the materials with different stress-strain behavior the best way is you go to the kitchen look at different things you have look at how the honey moves in comparison to water, look at how the mayonnaise move in compare it is a comparison to say a solution of a cornstarch, how the yogurt moves in comparison to milk and so on.

All of these so a very unique kind of characteristics of flow which can be classified into various classes but each of them has certain material properties like viscosity and so on that can be understood if we do a Rheology or experimental Rheology of those systems. I want to add the word experimental here because as opposed to what we have discussed for the most of this course in this part we want to really look at the experimental aspects of things more than compared to the theoretical aspects. How do we start from an experiment and then go back and analyze different systems we using simpler theories or empirical models that we can use to analyze the rheological behavior. This is how it is different so before I go into the idea of Rheology I first want to talk about the complex fluids in general and what are the classifications of different kinds of flow behavior that you can see something that you may have seen in your fluid mechanics class.

So, typically if I want to know the complexity of a fluid what I can do is look at the behavior under the application of an applied stress that of course give rise to some shear rate as long as it is a liquid. If it is for example a solid I would be interested in the amount of shear that stress causes. So, this is my stress versus shear rate which is what I used to characterize liquid and this is my stress versus shear which is what I used to characterize solid and then what we have are also the plots of the effective material parameters that we could get in these two cases. So, if I am interested in a liquid we typically talk about a viscosity as a function of shear rate and if I am interested in a solid I talk about some sort of an elastic modulus as a function of the applied shear and then different materials so different behavior.

So, when we call a material Newtonian liquid it has a straight curve here. The slope of which characterizes the viscosity η this is what is called a Newtonian liquid that follows the law τ as a constant term, η multiplied by $\dot{\gamma}$ and this will give you something like a straight line here because the viscosity is not changing by application of shear rate the viscosity remains to be the same and things like a water is a good example of a Newtonian liquid.

$$\tau = \eta \dot{\gamma}$$

Then there are class of liquids which basically thickens when we apply flow that means the viscosity increases when we apply shear as we increase the shear rate the viscosity increases and then there are materials or liquids that basically thins or viscosity decreases as we increase the shear rate. So, the things were for which you see a thinning behavior is known as shear thinning liquids and then this will have a behavior like this here if you see shear thinning and then for materials or liquids for which the viscosity increases is given like this just shear thickening and for these materials you see something like that.

So one of the ways to characterize the shear thinning and shear thickening behavior is what is known as a power law model that is we write τ where τ something like $\eta \acute{\gamma}^n$ this η is not the viscosity anymore. So, let us use a slightly different notation here just to be clear that this is not a constant viscosity let us call it some μ. The key issue now is that depending on the power of n you can get a shear thinning behavior or a shear thickening behavior. So, what we can write this is as some sort of in the power law model I can write as-

$$\tau(r)=\eta(\acute{\gamma})\acute{\gamma}=\mu\acute{\gamma}^{n-1}$$

So, now you can see when n = 1 then we get μ that is constant so we have a Newtonian liquid. When n is higher than 1 then we get η as μ $\acute{\gamma}$ to a power that is higher than 1. So, as I increase $\acute{\gamma}$ the viscosity will actually increase so it is a positive power of gamma dot so as I increase n to beyond 1 let us say if it is 1.1 then it is $\acute{\gamma}$ to the power .1 it is a positive power. So, this will increase with increase in $\acute{\gamma}$. So, this will be the shear thickening behavior.

$$n>1\equiv\eta(\acute{\gamma})=\mu\acute{\gamma}^{¿0}$$

Similarly when n is less than 1 then we will have η $\acute{\gamma}$ = μ $\acute{\gamma}$ to a power that is less than 0 and this will of course decrease with increasing $\acute{\gamma}$ so this will so a shear thinning behavior.

So, this is my so both of this I am representing using μ $\dot{\gamma}_n$ and I can define the effective viscosity using this particular formula.

$$n<1 \equiv \eta(\dot{\gamma}) = \mu \dot{\gamma}^{¿0}$$

Now there are also materials that will not really flow if I apply a small force they only start flowing when we apply a force beyond certain threshold. Think of toothpaste for example if I apply say a very small force on the tube nothing will come out only when I apply sufficient force on the tube the toothpaste start coming out. These materials are what we call are materials that have what is known as a yield stress. So, for a smaller stresses they will not really flow only for large stresses they will flow. So, these materials again can show behavior that would be something like this. This is what is called a Bingham plastic, once they start flowing their viscosity will be constant if it is like this but then it can also be like shear thinning beyond the yield stress shear thickening beyond the yield rest stress. So, until the yield stress τ_0 that we have defined that is this particular point the material does not flow only after that it starts flowing and even after that the viscosity may be constant may be decreasing with increasing shear rate may be increasing with increasing shear rate there can be a whole lot of possibilities okay this is why I am saying that even if you go to a kitchen or the daily use materials you will see all kinds of diversity and as we go towards polymer solutions and polymeric systems the diversity is simply increases because polymers are in between the solid and liquid and so they also saw some elastic behavior that is not typically given by the materials that we have just discussed.

Similarly when we look at a solid the same idea apply so we can have materials which are having a constant modulus this is called perfect elastic material. You can have materials that can so a behavior like this that is in the beginning you start with the high modulus and then as you keep on increasing the shear you eventually reach a state where material pretty much becomes a liquid that is what I call viscoelastic fluid and then finally you can have materials that can show a behavior like that where it starts from a high value as I increase here the magnitude of modulus decreases but does not quite go to 0 it does not become a liquid it remains somewhat solid still. This is the material I would call a viscoelastic solid. The reason why I use the word visco is because it is viscous it shows some liquid nature and it is elastic because it shows an elastic nature and then the final thing like solid or fluid that classification only tells you how much solid that is or how much fluid that is the whole point that there is a viscosity or a viscous nature indicates that the material has certain liquid nature how much is that is of course different depending on the material that we have.

So, let us say if you have a rubber ball that would be a viscoelastic solid but a gel will for example we are viscoelastic fluid or liquid. The same kind of a picture can be drawn here as well so this will be a constant modulus this is perfect elastic material then you can have other possibilities you can have something like this for a viscoelastic fluid and you may have something else for a viscoelastic solid.

So, the whole idea of Rheology is essentially to look at precisely this. So, we want to know how the stress versus shear rate profile looks like for the case of liquids, how the stress versus shear profile looks like for the case of a solid and how both of them look like for the case of a viscoelastic material and polymers are essentially polymer systems are essentially I would say almost always viscoelastic. So, we have to look at both τ versus $\dot{\gamma}$ and tau versus γ to look at the behavior because it cannot be characterized as a perfect solid or a perfect liquid.

So, all the experiments of Rheology basically centers around these ideas we want to get the viscosity as a function of shear rate or we want to get the stress as a function of shear rate or we want to get stress as a function of shear or we want to get the elastic modulus as a function of shear and if I do these experiments for different materials I can compare their properties and I can also by fitting into equations either derive constitutive equations or we can get the material parameters assuming certain constitutive equations this is what rheology does for you.

To start thinking about the idea of Rheology or the kind of rheological and I am talking about we can start with a very simple analogy starting from the high school physics that you have had let us say you have a tabletop and let us say you place a material on the tabletop and if I confine the material with another plate fixed at top and I start moving that plate using a weight that is connected through gravity. So, you apply a force on the plate and the plate is basically pulling the sample of material along with it.

So, now we can do two kinds of experiment in one experiment we will pull it at a constant rate that would give rise to a constant shear rate in the system or we can pull directly to a certain extension that will give you a certain amount of shear in the system. The only difference here is in one we are interested in the change or displacement in the sample in another we are interested in the rate of that displacement so, let us say if we pull it slightly and then we have a new position of the plate and that is giving rise to a new position of the sample that is the deformation that you are interested in. If I can measure how much is the amount of shear for a unit length of sample I can get the deformation for a certain shear if I do the same thing with time that is if I am shearing at a certain rate and I find the amount of shear divided by the time we get the shear rate and that would give me the force or stress I have to apply to pull at a certain shear rate.

So, the magnitude of force that I apply to get certain shear or shear rate or the magnitude of the shear that is caused by a certain force let say by gravity or the magnitude of shear rate due to certain force that may be gravity will tell you about the Rheology of the system. So, either I can fix weight and let it go down so in that case I do not have any control on the stress anymore. The stress is because of the tension in the rope this tension give rise to a certain stress here that is stress of course is per unit area.

So, in that case we are essentially fixing σ and we measure γ or $\acute{\gamma}$ depending on how the experiment is being conducted and we have a relation between σ and γ or σ and $\acute{\gamma}$ or σ and γ $\acute{\gamma}$ both depending on what kind of material we have. We may be interested in these 3 different experiments the first one I would do for a solid or a perfect solid the next one I will do for a liquid and the last one I will do for a viscoelastic material.

There is one more way of doing it that is I will fix the amount of shear or shear rate I want to achieve so we fix γ or $\acute{\gamma}$ and we measure the amount of force that need to be applied that is essentially measuring σ and again the end result will be the same that we will get a relation between σ and γ or σ and $\dot{\gamma}$ or may be both.

Now this is the kind of setup we really want the only problem is that there are some shortcomings with this particular setup. First of all you can imagine that let us say we have like a liquid sample and I starts acing like this in a plate if I want to go to say very high shear or very high shear rate we pretty much need a very long table because I am starting to pulling in this way and if I want to go to a very high shear I have to really need a very long, long table.

The other problem is like of course we have to have some way to confine the liquid somewhere because the liquid can really go haywire as soon as I start applying this force. If it is very thin liquid or let us say if it is an air then it is very difficult to control or confine the material within the two plates and we have to really find a way to counter this problem.

And third problem of course is like how exactly the experiment is being conducted we need to have a mechanism to find the force that being applied and just changing weight is probably not the best idea because the kind of resolutions we really want from the apparatus is much higher we want more accuracy in terms of the σ versus γ or σ versus γ profile because these are the constitutive laws I want to apply for various systems.

So, typically this is not what we do but the basic theme that we have to cause a deformation to the material and find the force required to cause the deformation or we can apply a certain force on the material and find the amount of deformation that is caused this is what really goes into any experimental rheology apparatus and the general word for those apparatus is Rheometer.

So, we will we will talk about how this Rheology experiments are conducted or how the Rheometers work in the next lecture. We will talk about like what kind of experiments are used to measure the constitutive to measure the stress shear or stress shear profiles and then to derive the constitutive laws or get the metrical parameters in the next lecture.

So, with that I conclude here, thank you.