Polymers Processing and Recycling Techniques
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Lecture – 79
Rheological Models

Hello, welcome to this week of lectures on polymer. We are in the 11th week where we are discussing topics related to polymer processing and recycling techniques. Having discussed properties and applications of various kinds, it's very important for us to understand what are the different techniques by which we actually process the polymers and achieve the final product that we would like and towards this one of the aspects that we have discussed is in terms of measuring the rheological properties of polymer melts and solutions as well as polymeric gels and in this lecture, we will focus on the rheological models and the focus will remain on concepts related to rheological modeling.

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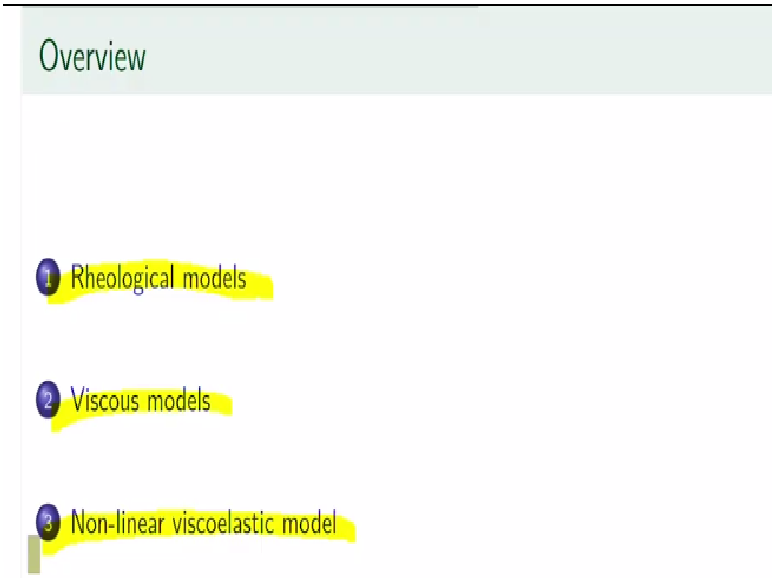

So we will look at some class of rheological models that are useful in order to describe the viscoelastic properties of polymeric systems. Then we will look at some examples of viscous models which are the simplest possible models and these have been known for 40-50 years and as a first approximation they can be used at times. However, given the computational power that we have these days and as we discussed, flow simulations and heat transfer simulations have become very important in terms of simulating, moulding or other processing operations. We these days use a lot of complicated model and we will therefore take a close look at one of such models.

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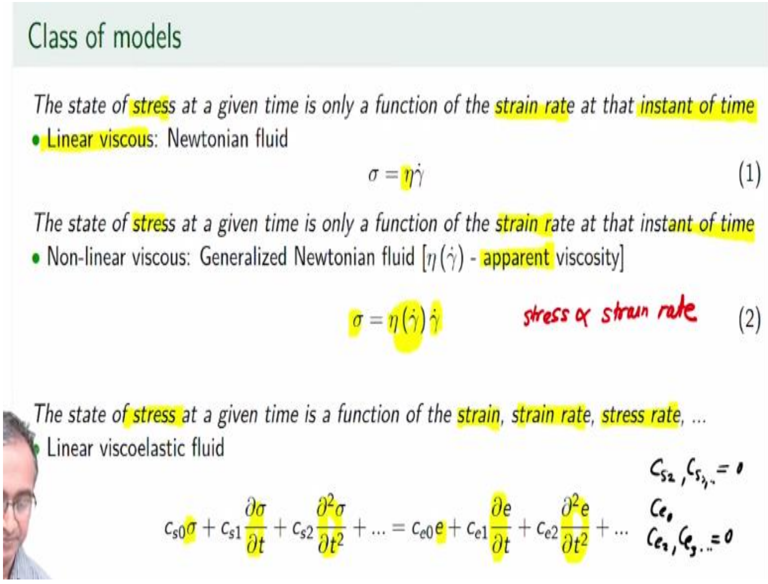

So the class of models that are generally available can be looked at from the point of view of energy storage and energy dissipation and energy storage of course we looked at in the context of solids where we looked at linear and non-linear elastic models. For fluids, we basically have the viscous models where the state of stress is only a function of strain rate at that instant of time. So stress is related to only strain rate and also the value of stress at a given instant of time is directly related to the strain rate at that instant of time. So, the example of this of course is in terms of most commonly known Newtonian fluid where it',s a linear model between stress and strain rate and the proportionality constant is viscosity. When we look at non-Newtonian fluids, one of the implications is that stress is no longer proportional to strain rate.

So in this case, still stress is a function of strain rate at that instant of time, but it is not a proportional function. So, therefore stress is related to strain rate but the proportionality constant itself is related to the strain rate and therefore we choose to call this viscosity now apparent viscosity, because it's no longer a material constant, but it is a material function and the material function varies as a function of strain rate. Shear thinning, shear thickening, pseudoplastic or dilatant these are examples of these non-linear viscous fluids or generalized Newtonian fluids. We call them generalized Newtonian because if you look at the structure of the equation, it still remains the same. It is still stress proportional to strain rate.

So, that general structure still remains the same. As we have seen in case of Voigt model or

Maxwell model or standard linear solid model, it's not only stress, strain and strain rate are related to each other, stress rate and so variety of quantities are involved in terms of relating stress and strain to each other, while in case of viscous fluid the instantaneous value of strain rate defines stress or vice versa. Instantaneous value of stress defines strain rate in the material. So the general viscoelastic fluid could be thought of as a material where state of stress is a function of strain, strain rate, stress rate and variety of other derivatives and the most general way we can write this is to say that stress is related to stress rate is related to rate of change of stress rate and related to strain, rate of change of strain and this is rate of change of strain rate and even higher order derivatives. So, this is the most general statement possible for a linear viscoelastic fluid that we can think of. Of course, if you put selective constants to 0, you can get Maxwell model or Voigt model or any such model. So, I don't know if you can spot Maxwell model in this, so for example if all the coefficients which are Cs2 and Cs3 and all of that, if they are all equal to 0 and similarly if C is 0 and Ce2, Ce3 these are all equal to 0, then I hope you can recognize by that what is Cs0 for Maxwell model, what is Cs1 for Maxwell model and what is Ce1 for Maxwell model. So do that exercise, you can see that all the viscoelastic models that we have discussed belong to this class of models.

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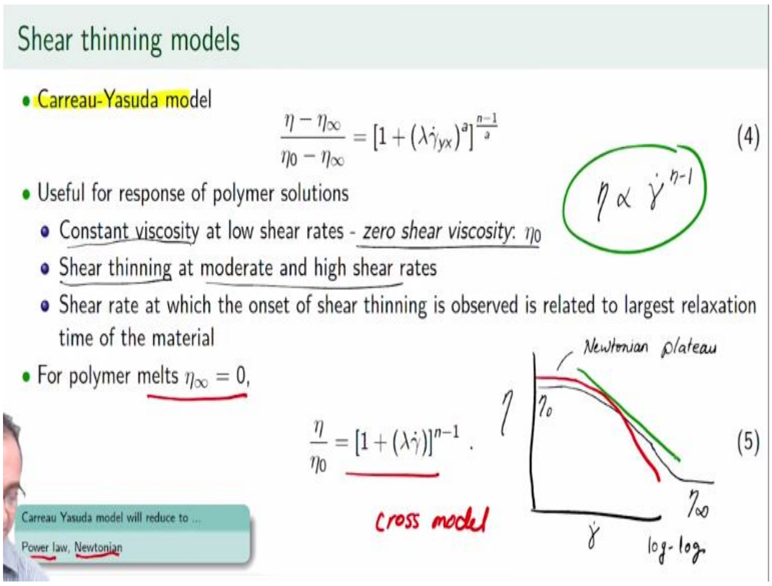

So let's look at a little bit more closely at some of the viscous models. Carreau-Yasuda model is one of the most commonly used model for describing the non-Newtonian nature of viscosity. It's a model which can describe shear thinning very well. So, the general response of the model is as follows that at so if we look at let's say stress as a function of strain rate, so we can look at stress as a function of strain rate, we can see that if strain rate is low, then viscosity is constant. So this is called the Newtonian plateau, so where viscosity is constant and so if we subject a polymeric melt to very low strain rates, it behaves like a Newtonian fluid where viscosity is constant. This is also called the zero shear viscosity. The zero shear viscosity is a very important determinant in terms of what is the entanglement in the material, what is the molar mass of the material, what temperature we are.

So looking at zero shear viscosity does give us some important clues about the structure of polymer. From polymer processing point of view, of course we need to know the viscosity at all different strain rates and so when strain rate is increased, then the shear thinning nature is obvious in case of polymer melts in solution and so shear thinning at moderate and high shear rates.

Carreau-Yasuda model also shows that at very high shear rates viscosity again becomes constant. So therefore, this is something which is observed in case of let's say a solvent. So η_∞ is related to the solvent viscosity, so at very high strain rates, we observe the behavior where all the chains are aligned in the flow field direction and therefore viscosity modification due to polymer addition is much less and so η_∞ is closer to the solvent viscosity. Of course, in case of polymer melts, what you often most of the time is some behavior like this.

$$\frac{\eta - \eta_\infty}{\eta_0 - \eta_\infty} = \left[1 + \left(\lambda \dot{\gamma}_{yx}\right)^a\right]^{\frac{n-1}{a}}$$

So there is only polymer melt and no solvent present, so there is only shear thinning observed, but there is a Newtonian plateau at lower shear rates. So for polymer melts, we can generally modify this model by setting η_∞ to 0 and then we get the simpler version of the Carreau-Yasuda model which also goes by the name of Cross model at times.

$$\frac{\eta}{\eta_0} = [1 + (\lambda \dot{\gamma})]^{n-1}$$

As an exercise, what you could do is try to see if you can set λ to be a large value or λ to be a small value or n to be equal to 1 what happens to it, this Carreau-Yasuda model. And I am sure you would be able to show that Carreau-Yasuda model will reduce to power law or Newtonian fluid model. Remember power law historically has been one of the most commonly used model for describing the shear thinning nature. All of these plots by the way are usually on a log-log scale. So many of the properties whether it is G′, G″ or stress-strain curves because we are looking at decades in terms of time scales. So we go for strain rate 10^{-3} to 10^4, frequencies we go from 10^{-4} to 10^3. So therefore, there are decades of time scales involved and generally these plots are always on a log-log scale. So if you have a power law which implies that η is related to strain rate, $\dot{\gamma}$ to the power n-1. So this particular slope will be exhibited. So this particular behavior would be exhibited just as a straight line, because it's a power law. So Carreau-Yasuda model can show all these different behaviors.

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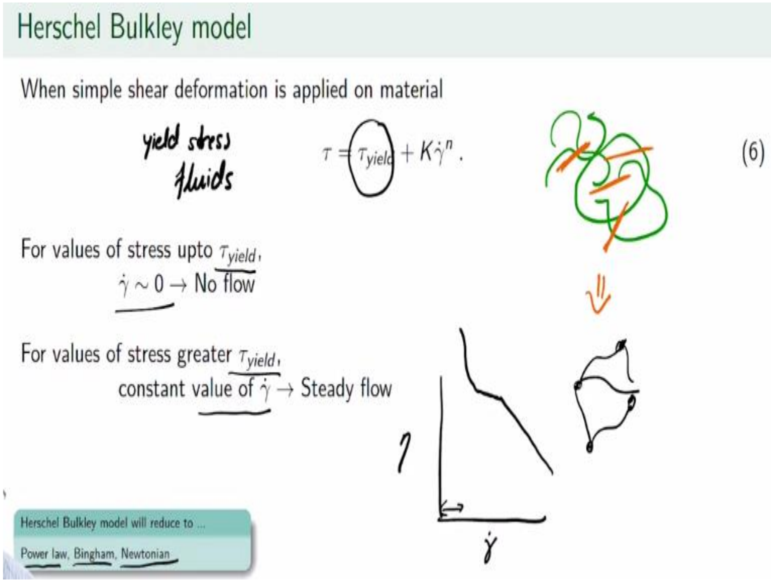

So, the other model which is very commonly used is called Herschel Bulkley model. This is a set of models which are useful for polymeric systems if there are fillers in it, because what happens is if you have the polymers with all their entanglements, if we allow shearing to happen at a very slow rate, then entanglements can slip past each other and therefore we get perfectly viscous behavior and therefore zero shear viscosity as constant viscosity.

But what if we now in this polymeric system put a set of fillers, let's say we put nanotubes or we put glass fibers. Then these glass fibers can start interacting with each other and they can act like network points, they can bridge the macromolecules with each other. So therefore, through interactions between glass fiber and glass fiber or through interaction between glass fiber and the macromolecule, this overall system ends up behaving like a system which is networked.

And what this implies is whenever the network points are strong, then we will not observe the viscous behavior, the fluid-like behavior, but this would start behaving like more solid like,

like a crosslinked rubber kind of a system. So therefore, if you look at viscosity as a function of strain rate for these kind of systems, shear thinning is observed at higher strain rate, but when you go to lower frequencies or lower strain rates what happens is again viscosity becomes very high because this crosslink point makes the material respond like almost a solid and therefore there is an yield stress in the material.

So generally, up to certain strain rate there is no flow at all and beyond a certain strain rate because stress has exceeded the yield stress value, flow starts happening in the material and therefore these materials are called yield stress fluids. In fact, you can see that Herschel Bulkley model if I set τ_{yield} to be 0, then it becomes a power law kind of a shear thinning material.

So Herschel Bulkley model is a yield stress model plus shear thinning model and so for values of stress up to τ_{yield} there is no flow in the material and when the stress is greater than τ_{yield}, there is a constant value of strain rate which is reached and the material behaves like a shear thinning viscous fluid. So, this Herschel Bulkley model also you can do an exercise and show that it reduces to variety of simpler models. So, this is an overview related to the viscous model.

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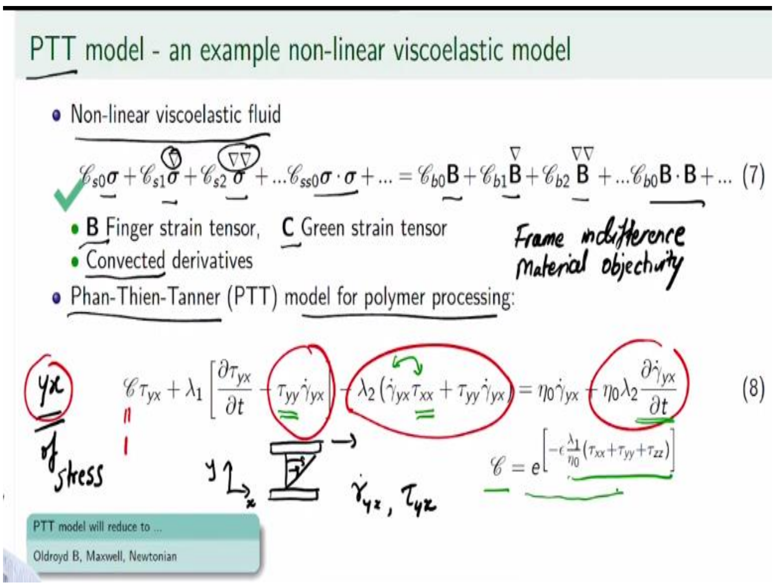

Now let's finish this lecture by looking at a non-linear viscoelastic model. Since this is an introductory course on polymer, we will not spend a whole lot of time because there is a course you can do on non-linear viscoelasticity of polymeric systems. But let's spend some time to understand how the non-linear models are not very different conceptually compared to some of the things that we have already discussed in such an introductory course.

So this is Phan-Thien-Tanner model which is one of the most commonly used model for polymer processing and any computational package that you get these days, you will see that this model is available as one of the menu for us to choose. Now, the linear viscoelastic model that we wrote where stress, stress rate, rate of change of stress rate, strain, strain rate so the same thing is valid for all large deformations or non-linear viscoelastic model also.

So if I were to write a very general mathematical relation describing a viscoelastic fluid for very large deformations and for non-linear deformation, then all I have to say is stress, stress rate, rate of change of stress, strain, strain rate, rate of change of strain rate and so on. Also, we may have stress multiplied by stress, so non-linear terms again. So, stress and stress square are related to strain or stress is related to strain and strain squared. So, this is an example of a non-linear model. Instead of using infinitesimal strain tensor or strain tensor which is valid only for small deformation we use these strains which we have discussed already when we discussed rubber and non-linear elasticity. These are called either finger strain tensor or green strain tensor and the rates that are evaluated are indicated using this symbol which is probably not familiar to most of you, so you do not have to worry about for this course purpose, but these are called convected derivatives.

Some of you might know that there is partial derivative, then there is total derivative, then there is material or substantial derivative. So, substantial derivative is evaluated by moving along with the material or it‘s also called we evaluate it in Lagrangian frame. So similarly, if we have to calculate stress rate, we must evaluate the derivative in what is called a convected frame, so, we get convicted along with the material, we get deformed along with the material.

So mathematically to be consistent in terms of getting a response where the material response doesn’t depend on how we define it or it’s also called frame indifference. So those of you who are interested could read more about what is meant by frame indifference, it is also called material objectivity. You can see the words objectivity and indifference. So basically, material response should not depend on how we describe it. So if we use this very simple physical notion and try to implement it in a mathematical sense where stress and strain and strain rate are all quantities which have 9 components, they are all tensors, then the convected rate definition automatically becomes one of the useful tools.

So therefore, non-linear viscoelastic models are described in terms of these convective derivatives. So let's stop here from the point of view of our course right now in terms of this discussion related to nonlinear viscoelastic model, but look at how the governing equation looks like for this PTT model for a simple shear flow. In terms of what we will look at is a situation where we let's say take the material between two parallel plates and therefore we have this rectangular coordinate system x and y and if we take this polymer melt which is a complicated material and shear it between parallel plates, then what we will have is $\dot{\gamma}_{yx}$ and τ_{yx} will be the stress components which are important.

So therefore, this is the yx component of stress for PTT model. I have said that you know because it is a tensor model, there are 9 components, but we will not worry about it but let's stare at this model and try to see how much more complicated non-linear viscoelastic model can get compared to models like Maxwell and other models. Now if you look at this model and I am just going to use some terms to indicate that you know if you drop these terms, then you will get back Maxwell model. So for example if this term is dropped out, this term is dropped out, and this term is dropped out and C =1, I hope you can spot that it is nothing but the Maxwell model. So any nonlinear viscoelastic model quite generally is an extension or more complicated terms compared to Maxwell model. But from our point of view other thing to notice is even though this is a yx component of stress, look at some of the other terms which are involved. So there is τ_{yy}. So the normal stress in y direction is also involved, normal stress in x direction is also involved, and there is a derivative of strain rate itself involved, there is also multiplication between stress and strain rate. So you can see that this is a much more complicated model and as this equation generally says that you know stress, strain rate and then multiplication of stress with stress, multiplication of strain with strain, multiplication of stress and strain rate, all of them are dependent, in fact PTT model which is one of the better known models of polymer processing has many of these terms.

Additionally, look at what the C is, C in fact involves τ_xx, τ_{yy} and τ_{zz} and it's a non-linear term again where it's an exponential to the power stress itself. Of course, the original arguments for developing a model such as PTT are due to the fact that polymers are heavily entangled system, there is only reptation motion possible when polymer molecules have to move and when we are trying to make them flow in polymer processing operations, chains get stretched but at the same time because of all these entanglements, there are only a number of ways in which the junction points which are the entanglement points can break and reform. So all of that is captured first using hypothesis and then a mathematical model is developed around it.

So PTT model is one of the successful models which is used for polymer processing. From the point of view of our seeking solutions if we are serious students of non-linear viscoelasticity, we have to understand these models, but at times if we are practitioners of polymer processing industry, we could use computational package, but it still is important for us to understand the models and various terms that are associated with such models.

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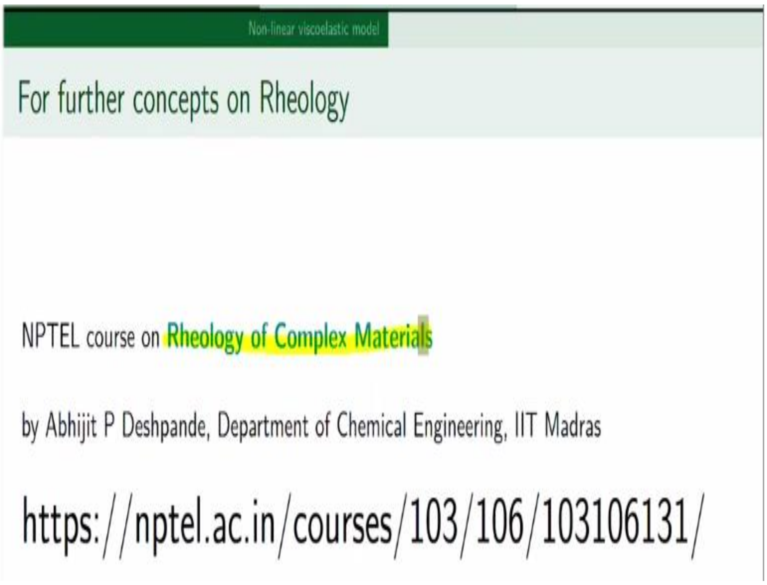

So with this, we will close this discussion related to rheological models. We have seen very simple models of viscous or some very complicated model of non-linear viscoelastic response and for those of you who are interested can take a look of a course which is by me also on rheology of complex materials and on YouTube, you will find various discussion related to nonlinear viscoelastic models also.

Thank you.