

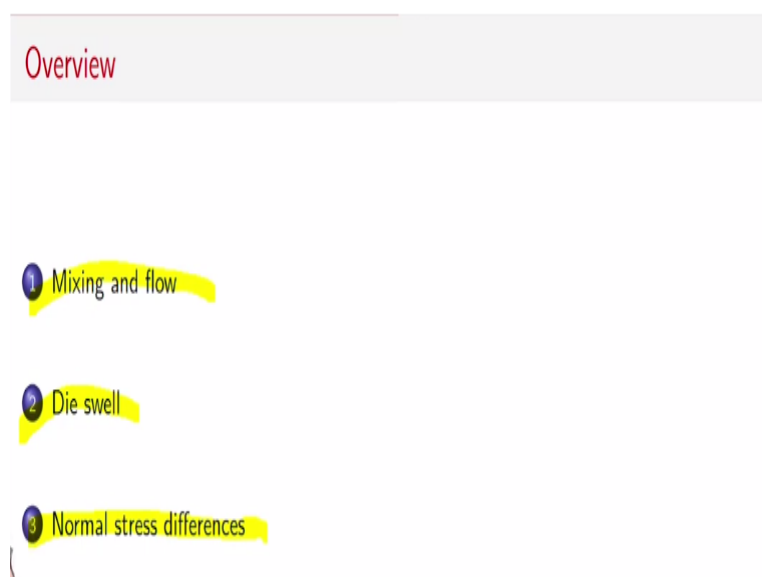
Polymers Processing and Recycling Techniques
Prof. Abhijit P Deshpande
Department of Chemical Engineering
Indian Institute of Technology - Madras

Lecture – 80
Rheology and Processing

Hello, welcome to the course on polymers and in these weeks we are discussing polymer processing and recycling techniques and you can see that we are spending significant amount of time, discussing various aspects of polymer processing recycling techniques, but in all of these discussions the macromolecular nature, the entanglement, the segments, the relaxation processes all of them form a very important component of our understanding how do we process these polymers.

So in this particular lecture, we will continue our discussion and try to relate rheology and processing by keeping a viewpoint of how it is useful in terms of applications.

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We will do this by first looking at what happens in terms of different types of flows that we have discussed and how is mixing done in case of polymers and how shear flow or extensional flow can be connected to what is the level of mixing that is happening in the polymers. A very practical application in terms of polymer processing is related to die swell or extrudate swell where the shape that is extruded out is related to the die, but it is not the same as what is the die opening.

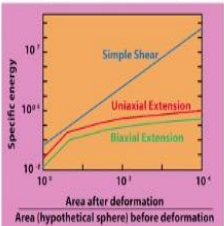
So how do we relate these to each other? And what we will see is one of the non-linear viscoelastic measure which is extremely important in terms of characterizing the polymer melt itself is normal stress difference. So viscosity and G' , G'' which are small deformation properties that we have discussed so far are no longer sufficient to characterize a polymer melt and explain phenomena like die swell. This will also highlight the fact that how a 1-dimensional picture is not at all sufficient when we are trying to discuss rheology and processing of polymeric systems.

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Mixing and flow

Mixing in different flows

- Laminar mixing, due to very high viscosity
- At a constant strain rate
 - Simple shear flow:
 - two material points separate linearly with time
 - Extensional flow:
 - two material points separate exponentially with time



(Utracki and Luciani, 2000)

So let's first look at mixing in different flows. One of the things we have to realize is the fact that polymeric materials are largely mixed in laminar flow condition. Whenever we mix low viscosity fluids, we achieve turbulence when all these eddies form and re-break and mixing is easily achieved. Of course, when eddies are very small, in the end molecular mixing does become important but in case of polymers because we have laminar flow the mixing is always dependent on the type of flow which is there and in terms of laminar flow we could either do a shear flow or we could do an extensional flow. In fact, mixing is very different in these two cases and the reason for that is as follows, that if you take let's say a simple shear flow and if let us say I look at 2 points and see how they are separated in time.

So if you recall, this is moving slightly higher velocity than this, so basically there is a relative velocity between them and the flow rate is kept constant because this top plate velocity has a constant velocity, but the relative displacement keeps on increasing as a function of time. So

the two material points if we take they are separating with respect to each other linearly in time which means the distance between them increases linearly with time. If I look at 10 seconds, there is some distance, and if I look at 20 seconds the distance would have doubled. That's what we mean by a linear increase. It's some proportional increase if not double, triple, but it keeps on increasing by the same factor and therefore it increases linear with time. But if we take a look at the extensional flow in which case we stretch the material, and therefore material flows in this direction but it contracts from the other direction and so, in this case the separation is in fact exponential in time, because in these kind of flows the V_x is proportional to some strain rate constant and then position of the material.

So if we know that velocity is nothing but $\frac{dx}{dt}$, then it's proportional to x and so what you can get is $\frac{dx}{x} = \text{some constant} \times dt$, so you can see that it is an exponential. So the position of material particles as a function of time changes exponentially. Therefore, two material points which are separated at some distance their distance changes exponentially which means it increases rapidly and so in terms of mixing this is very useful. So we can see that in terms of using if mixing laminar regime, we need to have as much as possible extensional mixing and this is what is shown in the graph here where if you look at the specific energy because energy which is required for achieving a certain degree of mixing in the material we can measure the mixing by saying that you know if let's say I have some material in which I draw a hypothetical circle and now what happens to this shape of this circle as the material is getting deformed? The more this circle gets deformed, the more there is a chance of one fluid layer contacting another fluid layer.

So therefore, area after deformation and area before deformation of this hypothetical sphere can give me an idea of what is the amount of mixing that can happen. And what you can see is in simple shear flow the energy required is much more, because particles which are close to each other do not really get separated, they are only separating linearly in time, but extensional flows can require much less amount of energy but this area under deformation increases quite rapidly. So therefore, extensional mixing is always better and this is achieved sometimes by choosing an appropriate processing technique.

So for example, when we use roll mills or when we use the twin screw extruders, so we achieve some of these features so that mixing is enhanced. The other feature that we ought to remember about the overall importance of viscosity being very high, not only do we get laminar flow but

we also get very high in terms of viscous dissipation, because viscous dissipation is just related to stress*strain rate, so the consequence of viscosity being very high is also we get lot of viscous dissipation and heat transfer is always important in case of polymer processing operations. So, we can see how rheology has a very important role to play practically in terms of deciding conditions for polymer processing, mixing, in terms of heat transfer during processing.

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Die swell or extrudate swell

Die swell or Extrudate swell

- Stretching and orientation of macromolecules
- Recovery
- Entanglements, reptation, ...

Correlation with a rheological property:

$$\frac{D_{ext}}{D_{ext0}} = K_{ext} + \left(1 + \frac{N_f^2}{8\sigma_w^2}\right)^{1/6}$$

normal stress difference (1)
shear stress, wall

Controlled dimensions of the extrudate, sharkskin effect, melt fracture, ...

→ Rheological and interfacial properties

Now, let's look at one last aspect related to importance of rheology which is based on the extrudate swell. So the fact that if we have a die opening which is let's say circular, if the material comes out of this die, its shape will be not at all circular, so it's going to be much more complicated. So if I want a fiber where the circular cross section is desired, then I will have to design a die which has a different shape. So we need to understand what is the extrudate shape compared to the die shape itself. However, there is another important phenomenon which is regardless of the shape itself the size which we get, the size of the die, so the nominal diameter of the die and the nominal diameter of the extrudate swell.

This is something when we open a tap of water and so if we have a tap of water and if we open it, then what happens is water falls out and generally the jet diameter is same order of magnitude or smaller than the diameter of the tap.

But in case of non-Newtonian fluids if we have this kind of a die opening from which the polymer melt is coming out, generally the diameter of the polymer melt is much more than the capillary or the die diameter and that's why we call it a swell. So the size of the extrudate itself

is much more different than whatever is the opening, through which the polymer is coming out. The reason for this is again related to same things that we have been blaming polymer behavior on and that is stretching and orientation of the segments of macromolecules.

So given that we have these macromolecules coil-like shapes and now we are forcing them to get sheared, what happens is the macromolecule segments get stretched and they start orienting. So in this part of the capillary or this part of the die where we are forcing the polymer molecule what you will see is the macromolecules are more oriented towards the flow direction, they are of course still entangled but on an average they are getting oriented but as soon as they come out and if you look at now the extrudate swell this region what happens is they would like to go back. So there is always a recovery and this is related to the fact that macromolecular conformation would like to be maximum and so there is a recovery related to the macromolecular coil shapes and so there is this swell. What you can also see is largely we are imposing shear stress on the material in this capillary. So this is something where it is mostly shear.

So even though we are forcing material in a pipe or a die and largely using shear forces, the material feels normal forces because it is getting stretched and there is a tendency for this stretch to recoil or recover, so the material develops what is called a normal stress in the material. This is very important discovery during the development of rheology as a field and people trying to understand polymer processing much better, that the diameter of the extrudate or the diameter of the extrudate when let's say it is a just a Newtonian fluid is related to each other through a coefficient which is related to normal stress difference in the material. So N_1 is called the normal stress difference and since there is a subscript 1, this is called the first normal stress difference. So that implies that there are two normal stress differences and I will explain that in a couple of minutes and then also there is the shear stress at the wall.

$$\frac{D_{ext}}{D_{ext0}} = K_{ext} + \left(1 + \left(\frac{N_1^2}{8\sigma_w^2} \right) \right)^{\frac{1}{6}}$$

So, this kind of a correlation is extremely useful for engineers. If I want to understand how much is the die swell in the material and if I look at you know if I have two melts with different viscosity, there is no way I can explain why the two have different die swell. It could also be that two materials have different viscosity but they have exactly the same dies well. So, what

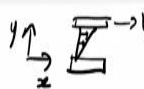
is determining the die swell property? The die swell property is depending on the stretching and recovery. And recovery and stretching are related to the elasticity of the material and elasticity is also associated with this normal stress difference. So therefore, the ratio of the normal stress difference to what is the shear stress in the material determines how much will be the die swell. And this kind of a correlation then tells us that we must understand normal stress differences at a fundamental level because they are part of very practical correlations.

And the reason of entanglement, reptation, the overall structure that we have discussed so many times for the polymeric systems are very important in terms of determining their rheological response, in terms of normal stress differences and these normal stress differences have immediate implications for practical usage, where we can understand die swell by characterizing normal stress differences in the materials.

Therefore, if our objective is to get control dimensions of the extrudate, we must understand normal stress differences in the material. Over and above this if there are various interfacial properties, interfacial tension, surface tension which determine several other key features of polymeric melt behavior. For example, if our objective is to produce a nice smooth cylindrical object like this if there is lot of undulations on the surface then it is a failed part, failed processing operation. So things like sharkskin effect or melt fracture which will actually completely damage the overall surface of the extruded material are not desirable at all. So rheology and interfacial properties both have to be understood if these advanced failure phenomena during polymer processing have to be understood. So for our course, we are not going to go into details of these but we should remember that many of the things we have discussed in terms of rheology and processing we have discussed those set of rheological properties which can tell us information about what flow rate to use, what may be the pressure drop, what is the effective viscosity, what is the overall dissipation rate and these kinds of features related to polymer processing. However, there are several other features which have to be understood before we become successful polymer processing people.

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Deformation in simple shear flow

Velocity $v_x(y) = \dot{\gamma}_{yx} y$  (2)

Velocity gradient $\text{grad} \mathbf{v} = \begin{bmatrix} \frac{\partial v_x}{\partial x} & \frac{\partial v_x}{\partial y} & \frac{\partial v_x}{\partial z} \\ \frac{\partial v_y}{\partial x} & \frac{\partial v_y}{\partial y} & \frac{\partial v_y}{\partial z} \\ \frac{\partial v_z}{\partial x} & \frac{\partial v_z}{\partial y} & \frac{\partial v_z}{\partial z} \end{bmatrix} = \begin{bmatrix} 0 & \frac{\partial v_x}{\partial y} = \dot{\gamma}_{yx} & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}$ Shear rate (3)

Strain rate tensor $\mathbf{D} = \frac{1}{2} \begin{bmatrix} 2 \frac{\partial v_x}{\partial x} & \frac{\partial v_x}{\partial y} + \frac{\partial v_y}{\partial x} & \frac{\partial v_x}{\partial z} + \frac{\partial v_z}{\partial x} \\ \frac{\partial v_y}{\partial x} + \frac{\partial v_x}{\partial y} & 2 \frac{\partial v_y}{\partial y} & \frac{\partial v_y}{\partial z} + \frac{\partial v_z}{\partial y} \\ \frac{\partial v_z}{\partial x} + \frac{\partial v_x}{\partial z} & \frac{\partial v_y}{\partial z} + \frac{\partial v_z}{\partial y} & 2 \frac{\partial v_z}{\partial z} \end{bmatrix} = \frac{1}{2} \begin{bmatrix} 0 & \dot{\gamma}_{yx} & 0 \\ \dot{\gamma}_{yx} & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}$ (4)

So, let's continue and understand very briefly what is normal stress difference. We will do this by looking at simple shear flow which is again nothing but just taking fluid between two parallel plates and making them move. One of the plates is moving with some velocity, v and therefore the overall fluid moves and this is with this coordinate system x and y we say that velocity is there in x direction it is only a function of y . And due to this velocity, there is basically only one component of velocity gradient and this we call the shear rate. If you look at the overall strain rate tensor, it has only two components which is directly related to shear rate, but notice that so many components are 0. So normal components are 0, and also components which are related to z and xz , yz they are all 0.

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Stress tensor in simple shear flow

- Stress tensor in rectangular coordinates

$$\begin{bmatrix} \sigma_{xx} & \sigma_{yx} & \sigma_{zx} \\ \sigma_{yx} & \sigma_{yy} & \sigma_{zy} \\ \sigma_{zx} & \sigma_{zy} & \sigma_{zz} \end{bmatrix} = \begin{bmatrix} -p & 0 & 0 \\ 0 & -p & 0 \\ 0 & 0 & -p \end{bmatrix} + \begin{bmatrix} \tau_{xx} & \tau_{yy} & \tau_{zx} \\ \tau_{yx} & \tau_{yy} & \tau_{zy} \\ \tau_{zx} & \tau_{zy} & \tau_{zz} \end{bmatrix}. \quad (5)$$

- For Newtonian fluid or for non-linear viscous / Generalized Newtonian fluids

$$\begin{bmatrix} \tau_{xx} & \tau_{yx} & \tau_{zx} \\ \tau_{yx} & \tau_{yy} & \tau_{zy} \\ \tau_{zx} & \tau_{zy} & \tau_{zz} \end{bmatrix} = 2\mu \left(\frac{1}{2} \begin{bmatrix} 0 & \dot{\gamma}_{yx} & 0 \\ \dot{\gamma}_{yx} & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} \right) \text{ or } = 2\eta(\dot{\gamma}_{yx}) \left(\frac{1}{2} \begin{bmatrix} 0 & \dot{\gamma}_{yx} & 0 \\ \dot{\gamma}_{yx} & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} \right). \quad (6)$$

τ_{yx}, τ_{zy}

Now for this kind of a situation if we look at what happens to stress, stress also only those components are nonzero wherever strain rate is nonzero. So therefore, τ_{yx} or σ_{yx} , σ is the total stress, τ is the deviatoric stress. So generally, what we see is only τ_{yx} is nonzero and therefore σ_{yx} is nonzero, but σ_{xx} and σ_{yy} are nothing but $-p$.

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Stress tensor in simple shear flow for viscous fluids

- Total stress tensor

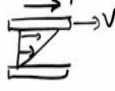
$$\begin{bmatrix} -p & \tau_{yx} & 0 \\ \tau_{yx} & -p & 0 \\ 0 & 0 & -p \end{bmatrix}$$

Normal stresses are identical = $-p$ (7)
- Deviatoric stress tensor

$$\begin{bmatrix} 0 & \tau_{yx} & 0 \\ \tau_{yx} & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}$$

Normal stresses are zero. (8)
- Normal stress differences are zero

$$\sigma_{xx} - \sigma_{yy} = \sigma_{yy} - \sigma_{zz} = 0 ; \tau_{xx} - \tau_{yy} = \tau_{yy} - \tau_{zz} = 0.$$



So in this situation if I look at what happens to normal stresses. So if I look at the total stress tensor, normal stresses are all equal to $-p$. They are identical and they are equal to $-p$. If I look at the deviatoric stress tensor, normal stresses are all 0. So normal stress difference is 0 in case of a Newtonian fluid when we are imposing shear flow on it. What that implies is also that if I have this simple shear flow and because I am moving the top plate with a certain velocity, I have to apply a certain force on it and so I need to apply a force to make this velocity possible and that is all that is required for the velocity to be kept constant for a Newtonian fluid. In fact, same feature is also observed for shear thinning fluids. In case of shear thinning fluids also what you can see is generalized Newtonian fluids only the yx component is nonzero and so therefore for both linear viscous fluids and non-linear viscous fluids or Newtonian fluid and generalized Newtonian fluid normal stress differences are 0.

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Stress tensor in simple shear flow for a viscoelastic fluid

- Total stress tensor

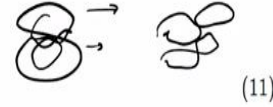
$$\begin{bmatrix} -p + \tau_{xx} & \tau_{yx} & 0 \\ \tau_{yx} & -p + \tau_{yy} & 0 \\ 0 & 0 & -p + \tau_{zz} \end{bmatrix}$$

Normal stresses arise in simple shear flow. (10)



- Deviatoric stress tensor

$$\begin{bmatrix} \tau_{xx} & \tau_{yx} & 0 \\ \tau_{yx} & \tau_{yy} & 0 \\ 0 & 0 & \tau_{zz} \end{bmatrix}$$



- Normal stress differences

General definition: 1 is the direction of flow and 2 is direction of shear

$$N_1 = \tau_{11} - \tau_{22} = \sigma_{11} - \sigma_{22} ; N_2 = \tau_{22} - \tau_{33} = \sigma_{22} - \sigma_{33} .$$

But let's look at the situation for a viscoelastic fluid. In case of a viscoelastic fluid, what happens is even τ_{xx} , τ_{yy} , and τ_{zz} are nonzero even though we are only imposing shear flow and practically what that implies is, if I take a viscoelastic fluid between two parallel plates and like earlier, I impose a certain velocity of the top plate so that fluid starts moving. I have to apply a force so that this plate motion is possible, but in addition to this force I also need to apply a normal force on the material. Can you think of where does this normal force come from? Why is there a tendency of this fluid to throw the plates away even though I am only trying to move the plate horizontally? So if we let's say just choose a coordinate system and I will state it again, so the plate is being moved only in x direction, but the polymeric material seems to deform and make the plate move in the y direction and that's why to keep the gap the same I will have to apply a normal force and ensure that the gap is the same so that the strain rate which is nothing but V by H remains constant for this particular experiment, which is a simple shear flow at a constant strain rate. So, therefore this is a very practical implication that you know even though the motion is largely in x direction, the material generates stresses which are not just shear stresses but normal stresses and these normal stresses lead to this normal force N .

So if I can do rheology like earlier where I rotate and therefore a torque is required to rotate this material and shear between two plates or cone and plate, if I can measure the normal force which is this material generates, then I can have a measure of the normal stresses in the material. And again you can think what is happening at a macromolecular scale because at equilibrium macromolecules are coil like but because we start shearing them what happens is

they start getting stretched and because they got stretched, there is a tendency for them to recover and that is what leads to the normal stress differences. So deviatoric stress also therefore will have the normal stresses and we can define the two normal stresses based on whatever are the flow direction and direction of shear. So in this example, x is the direction of flow and y is the direction of shear, y is the direction in which there is velocity gradient.

So in the example of a simple shear flow discussed here, N1 will be $\tau_{xx} - \tau_{yy}$ and N2 will be $\tau_{yy} - \tau_{zz}$ or $\sigma_{yy} - \sigma_{zz}$ and $\sigma_{xx} - \sigma_{yy}$. This N1 is what is related to die swell in the material. So I can do this very useful experiment, I do simple shear just the way I did for measurement of viscosity, but in addition to focusing only on the force which is related to shear stress I also focus on the normal force which is related to normal stress difference, measure it, and then I know how to predict die swell for a given polymeric material.

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Different techniques of rheology

- Rotational rheometers
- Tube flows
 - U tube viscometers, Ubbelohde viscometer
 - Capillary rheometers
- Extensional rheometers
- Trade tests
 - Melt flow indexer
 - Mooney viscometer
 - Oscillating disk rheometer (ODR) and moving die rheometer (MDR)
 - Penetration test

} pressure
pressure drop vs flow rate

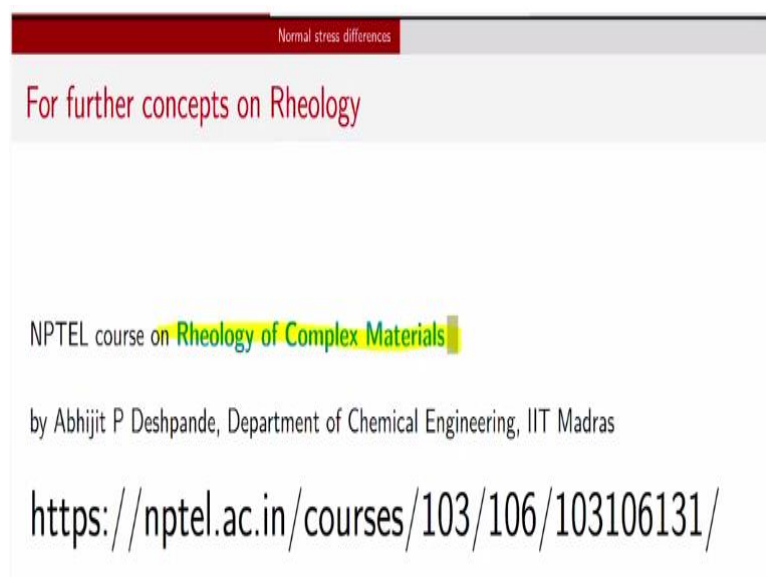
So, with this one of the features that you can see that once to understand rheology, 3-dimensional picture is always required. Now we will close this lecture by just pointing out that lot of things we have discussed so far are related to rotational rheology where we take material between different plates and or cone and plate or different concentric cylinders and then achieve a Couette flow.

However, we can also do tube flow where we do apply pressure and there is a pressure drop and flow rate measurement which can again give us idea of the viscosity of the material and capillary rheometers are extremely common in terms of polymer processing operations. On the

other hand to understand viscosity for dilute solutions, polymer solvent systems, to understand solution behavior we use U-tube viscometers and Ubbelohde viscometers where viscosity is slightly modified compared to solvent and therefore these are low viscosity systems. Given that we have seen how important extensional flow is for polymer processing operation, there are fair number of extensional rheometers which have come into being in the last 15-20 years. Initially in 80s and 90s, this was a very difficult set of experiments to do. Now they have become easy and many commercial rotational rheometers also offer these days' extensional attachments.

Again, 3-dimensional picture is must to understand the extensional versus shear geometry of polymeric systems. Of course, we have also seen that to complement these and to get some quick numbers we have the Mooney rheometers and the oscillating disk rheometers and melt flow indexes which are very useful tools for practitioners to generate some numbers to make some quick design decisions.

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Normal stress differences

For further concepts on Rheology

NPTEL course on Rheology of Complex Materials

by Abhijit P Deshpande, Department of Chemical Engineering, IIT Madras

<https://nptel.ac.in/courses/103/106/103106131/>

So, with this we will close this lecture and if you are interested in knowing little more about normal stress differences and how to understand them for not just polymeric systems but for filled polymer systems and for colloidal systems, you can look at these lectures. Thank you.